

SOME REACTIONS OF ACETYLENE

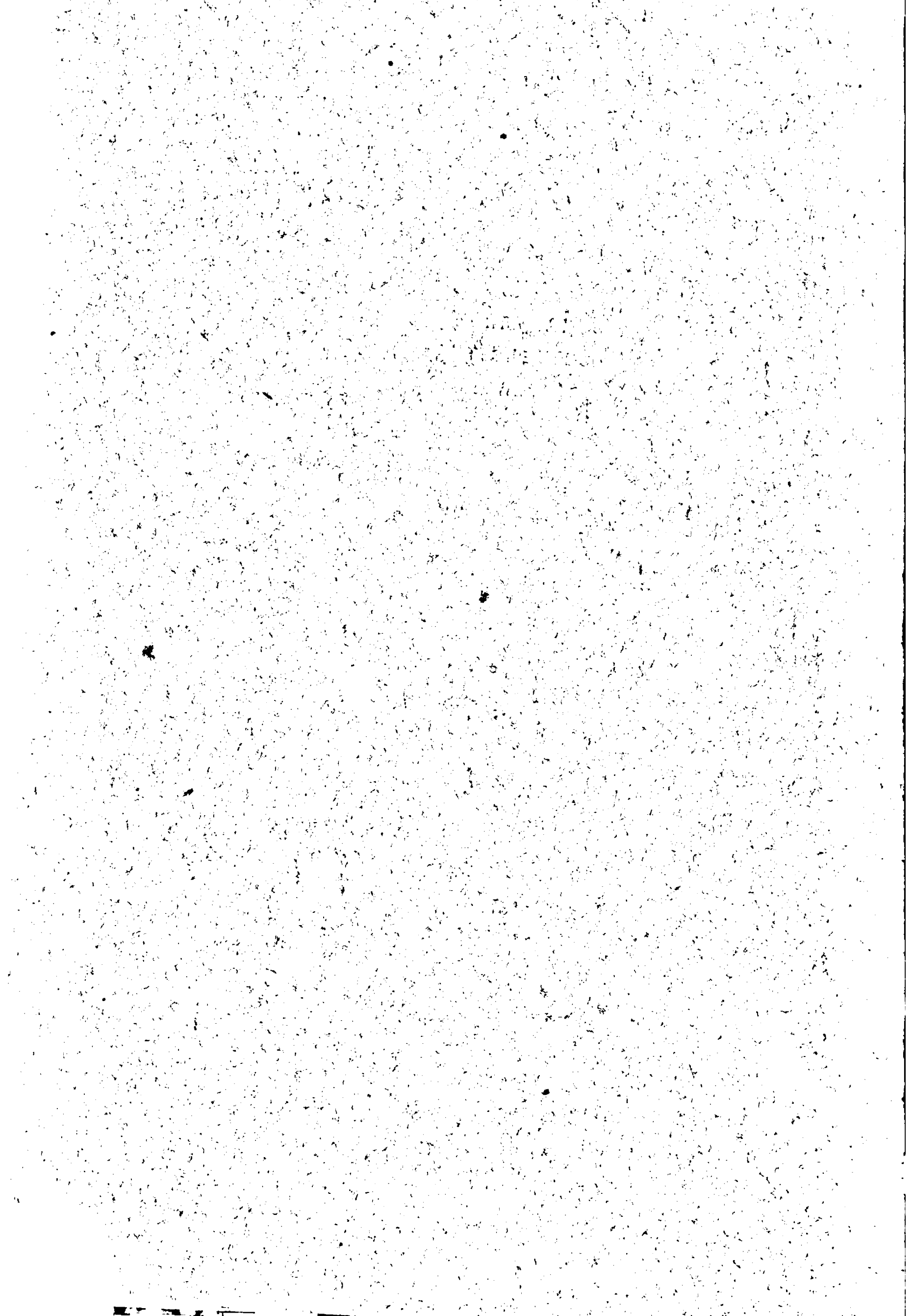
DISSERTATION

SUBMITTED TO THE FACULTY OF PHILOSOPHY OF THE CATHOLIC UNIVERSITY OF AMERICA FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

BY

JULIUS A. NIEUWLAND, C. S. C.

NOTRE DAME UNIVERSITY PRESS
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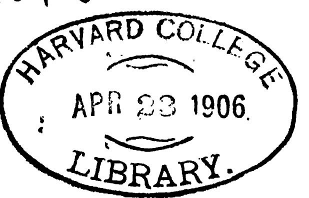
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The work about to be described was suggested by Prof. John J. Griffin and carried on under his guidance. I express to him my sincere thanks for the kind counsel and instruction received during my course of chemistry at the Catholic University. I gratefully acknowledge my obligations also to Prof. E. Greene, Prof. E. Pace, and Dr. T. Shields, under whom I pursued my studies in botany, experimental psychology, and biology respectively.

THE HYDROGENATION OF ACETYLENE.

THE HISTORY OF THE SYNTHESIS OF ETHYLENE

Numerous attempts have been made to unite acetylene with hydrogen to form ethylene or ethane. The first combination of acetylene with hydrogen was effected by Wilde,[1] who united them by passing the gases over platinum black, ethylene being formed. The residual gas did not give the acetylene reaction with ammoniacal cuprous chloride, and was absorbed by fuming sulphuric acid.

Berthelot[2] succeeded in obtaining ethylene from acetylene given off from copper acetylide in the presence of nascent hydrogen. The gases were obtained from zinc and from copper acetylide in ammonia water. Hydrogen from an acid solution did not give a good yield of ethylene. The ethylene was separated from the acetylene with difficulty, as the two hydrocarbons dissolved in the ammoniacal cuprous chloride. The latter gas, however, formed a precipitate of copper carbide, from which the acetylene could be determined gravimetrically, and the ethylene could be calculated volumetrically by boiling the solution of the cuprous chloride, when the gas was evolved from the solution, and measured after washing free from ammonia.

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[1] Ber. 7. 353. (Bull. d' Acad. Royal de Belg. 2, XXI., No. 1. (1864).

[2] Ann. Chim. Phys. 3, LXVII., 51, (1863.)

Berthelot[1] likewise showed that when a mixture of hydrogen and acetylene was heated, ethylene was one of the products. He accounted for the formation of the ethylene in two ways, first by direct addition, when the action represented by the equation, $C_2H_2+H_2= C_2H_4$, took place. As, however, the yield of the ethylene was too small to correspond to this reaction, another mode of formation was suggested, namely: $2C_2H_2 = C_2H_4 + 2C$. Ethylene likewise underwent decomposition into acetylene and ethane: $2C_2H_4 = C_2H_2+C_2H_6$. If hydrogen were present it united with the ethylene to form ethane.

In 1895, N. Caro[2] claimed that he had obtained alcohol from acetylene. This gas and hydriodic acid gave ethylene di-iodide, or ethylidene di-iodide, and this product being boiled with a concentrated solution of caustic potash gave potassium acetate, acetylene and alcohol. Seventy grams of alcohol were said to have been obtained in one operation. When the di-iodide was decomposed with silver hydroxide, only small quantities of acetylene were obtained, together with 90 per cent. potassium acetate and alcohol. (!) The di-iodide of ethylene heated in closed tubes with water gave a yield of alcohol that amounted to 40 per cent. of the theoretical.

Krüger and Pueckert[3] repeated Caro's work, and found that they could make 50 grams of di-iodide in three months and from this no alcohol could be obtained, though aldehyde was shown to be present.

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[1] Ann. Chim. Phys. 4, IX., 431.

[2] Cent. (1895) 2, 437. Chem. Ind. 18, 226.

[3] Chem. Ind. 18, 454.

Caro repeated his work, but could not obtain his previously published results and acknowledged his mistake.

Krüger[1] could not, moreover, succeed in uniting acetylene with nascent hydrogen, as Berthelot[2] had claimed. In 1894, an article was published by Frank[3] advocating the commercial manufacture of alcohol thus prepared by the action of acetylene on nascent hydrogen. The ethylene formed was to be led into ordinary strong sulphuric acid. This, diluted and boiled with water, would give alcohol. The acid would be again concentrated and used. This process was represented by the following reactions:

$$C_2H_2+H_2=C_2H_4,$$

$$C_2H_4+\begin{matrix}HO\\HO\end{matrix}>SO_2=\begin{matrix}C_2H_5O\\HO\end{matrix}>SO_2,$$

$$\begin{matrix}C_3H_5O\\HO\end{matrix}>SO_2+HOH=\begin{matrix}HO\\HO\end{matrix}>SO_2+C_2H_5OH.$$

In 1899 and 1900, Sabatier and Senderens[4] studied the action of finely divided metals such as nickel, cobalt, copper, and iron on a mixture of hydrogen and acetylene, and found that under certain conditions of temperature and time, ethylene, ethane and

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[1] Chem. Ind. 18, 459.

[2] Compt. Rend. 54, 515.

[3] Chem. Ind. 18, 74. (1894).

[4] Compt. Rend. 128, 173, and 130, 1559, 1628, 1762.

other hydrocarbons of the aliphatic and aromatic series were obtained.

In 1902, the addition of hydrogen to acetylene was effected electrolytically by Bilitzer.[1] He electrolyzed acetylene gas dissolved in a solution of sodium potassium and ammonium hydrates, and in sulphuric acid. In the alkaline electrolytes depolarization with the union of acetylene and the electrolytic hydrogen took place with a platinized platinum cathode, but not with plates of platinum or nickel. In sulphuric acid solutions of acetylene with platinized platinum electrodes the products were ethylene, ethane, and hydrogen, according to the strength of the current used. The hydrogenation of the acetylene was effected only when very weak currents were employed. This seems to show that the action was entirely a mechanical one, for when strong currents were used the platinum electrodes would become coated with gas and prevent the access of the acetylene to the finely divided platinum on the surface of the electrode. The acetylene was absorbed with ammoniacal silver nitrate, the ethylene with fuming sulphuric acid. Hydrogen and ethane were determined by explosion. Bilitzer worked with very small quantities and claimed yields of ethylene and ethane entirely quantitative, measured by the law of electrochemical equivalents.

In a solution of normal sulphuric acid, alcohol was supposed to be formed at the mercury cathode, presumably due to the reduction of aldehyde formed by

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[1] Monats. f. Chem. XXIII., 203.

the action of the sulphuric acid on the acetylene. Traces of alcohol were vouched for. The alcohol was indicated by the potassium bichromate and iodoform reactions. The author wished to obviate any mistake and passed acetylene into a portion of the acid without using any current. Only the odor of iodoform was noticed. When the current was passed through the solution for the same length of time as in the previous experiment, a fine but perceptible precipitate of iodoform was obtained. Therefore the author concluded that in the second instance the precipitate of iodoform was due to the alcohol formed at the cathode. The author did not suppose that acetylene was changed to ethylene in an acid solution, but thought that the aldehyde present, especially at the mercury cathode was reduced to alcohol at that pole. Now this presupposes that the aldehyde was present before the alcohol was formed. Alcohol may have been present, but the iodoform test does not demonstrate its presence when a primary aldehyde is in solution with it. Acetaldehyde will give the iodoform reaction far more readily than alcohol,[1] and so no reliance can be put in this test. Bilitizer accordingly concluded that with platinized platinum electrodes depolarization takes place at the cathode, and that the products in an alkaline solution are ethylene, and ethane when low potentials are used. In a sulphuric acid solution with a cathode of mercury, small quantities of acetylene are changed to traces of alcohol. The improbability of this conclusion will be

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[1] Lieben,—Ann. Supp. 7,218 and 377.

more evident after considering the results I obtained in the electrolysis of various solvents with electrodes of calcium carbide.

In the December number of Electrochemical Industry of the year 1902, there appeared the review of a patent granted to J. W. Harris, for the manufacture of ether and alcohol, from acetylene by electrolysis. The method, briefly described, is as follows. Acetylene is introduced into sulphuric acid in a heated vessel, so that the gas passes under a conical cathode of metal. The acetylene is said to unite with the nascent hydrogen at the cathode to form ethylene. This unites with sulphuric acid to form ethyl sulphuric acid. The anode is contained in a porous cell to prevent the oxidation of the contents of the cell. When the electrolyte contains over fifty per cent. of water alcohol is formed. As the proportion of the water diminishes the formation of ether begins. Ethane may also be formed but this is to be prevented as much as possible. The formation of the products is thus accounted for :

$$C_2H_2+H_2=C_2H_4,$$

$$C_2H_4+H_2SO_4=\begin{matrix}C_2H_5O\\HO\end{matrix}>SO_2,$$

$$\begin{matrix}C_2H_5O\\HO\end{matrix}>SO_2+HOH=C_2H_5OH+H_2SO_4,$$

$$\text{and, } 2\begin{matrix}C_2H_5O\\HO\end{matrix}>SO_2+HOH=(C_2H_5)_2O+2H_2SO_4,$$

$$\text{or, } \begin{matrix} C_2H_5O \\ HO \end{matrix}>SO_2+C_2H_5OH=H_2SO_4+(C_2H_5)_2O.$$

It was suggested that the union of acetylene with nascent hydrogen might be effected at a cathode of calcium carbide in an electrolyte of appropriate dilution. Before proceeding to this attempt it was deemed necessary to determine the action of sulphuric acid on acetylene and calcium carbide, and whatever simple reactions might take place in such a cell. There is no record of any work done on the action of sulphuric acid on calcium carbide. Whatever work on acetylene has been done refers to the reaction of the gas itself with sulphuric acid.

The anode products of the electrolysis were studied by Coehn,[1] in 1901. When a solution of caustic potash was electrolyzed while a stream of acetylene was passed over the anode, formic acid was obtained. Sulphuric acid similarly treated gave acetic acid.

ACTION OF SULPHURIC ACID ON ACETYLENE.

That acetylene acted upon sulphuric acid was first perceived by Edmund Davy[2] who discovered the hydrocarbon. He says in the report of his discovery: "The new gas is absorbed to a certain extent by, and blackens sulphuric acid." Berthelot[3] first investigated the products of the reaction of strong sulphuric acid on acetylene. He obtained an acid, to

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[1] Zeits. f. Elect. 7, 681.

[2] Ann. 23, 144. (British Association Reports, 1836, 62.)

[3] Ann. Chim. Phys. (1863), 67, 560.

the barium salt of which he assigned the formula, $Ba(C_2H_3SO_4)_2$, and called it barium vinyl sulphate. He claimed that on boiling the acid with water, vinyl alcohol (C_2H_3OH) was formed as a decomposition product, in a way analogous to the formation of ethyl alcohol from ethyl sulphuric acid.

The experiments of Berthelot were repeated by Lagermarck and Eltekow[1] and also by Zeisel.[2] They found that no vinyl alcohol was obtained, but that the product was crotonaldehyde. They ascribed the formation of the crotonaldehyde to the condensation of acetaldehyde with sulphuric acid as Kekule[3] had shown in his attempt to synthesize an aromatic compound from acetaldehyde. According to these investigators the mechanism of the transformation of acetaldehyde may be represented by the following reactions:

$$C_2H_2 + HOH = CH_3CHO,$$

$$\begin{array}{l} CH_3CH\ O \\ \qquad CH\ H_2CHO = CH_3CH{:}CH\ CHO + H_2O. \end{array}$$

Zeisel, however, ascribed the formation of the crotonaldehyde which he found in his repetition of Berthelot's work to the presence of vinyl haloid impurities in the acetylene. The gas in all these experiments was produced from ethylene bromide, or the copper acetylide, both of which give some vinyl

[1] Ber. 9, 637, and 13, 693.
[2] Ann. 191, 366.
[3] Bull. Soc. Chim. (177), 287, 540. Ber. 3, 604, and Ber. 2, 365.

products. Zeisel claimed that in some of his experiments he had taken special precautions to eliminate these impurities, and then found that crotonaldehyde was not obtained. When purified acetylene was used, a syrupy sulphonic acid was obtained in small quantity.

In support of his contentions that vinyl alcohol was obtained from sulphuric acid and acetylene, Berthelot claimed that allylene, a homologue of acetylene, gave allyl alcohol with sulphuric acid. Schrohe[1] showed that this was ordinary acetone.

Berthelot[2] next tried the action of acetylene on fuming sulphuric acid, and found that an acetylene sulphonic acid was formed that was not decomposed on boiling in aqueous solution. The salt of this acid gave phenol when fused with caustic potash. Berthelot claimed that acetylene was simultaneously polymerized and oxidized by the caustic alkali. Crotonaldehyde similarly fused yielded no phenol but potassium acetate.

In 1898, Muthman[3] repeated Berthlot's work with fuming sulphuric acid and acetylene. He obtained methionic acid and explained its formation as due to the decomposition of an acid of the supposed formula: $\begin{matrix} CH(SO_2OH)_2 \\ | \\ CH(OH)_2 \end{matrix}$.

$$C_2H_2 + 2H_2SO_4 = \begin{matrix} CH(SO_2OH)_2 \\ | \\ CH(OH)_2 \end{matrix},$$

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[1] Inaug. Dissert. Tübingen, 1875. Ber. 8, 367.

[2] Ann. Chim. Phys. 4, XIX., 429, 1870. Ann. 154, 132.

[3] Ber. 31, 1880.

$$\begin{matrix} CH(SO_2OH)_2 \\ | \\ CH(OH)_2 \end{matrix} + SO_3 = CH_2(SO_2OH)_2 + CO_2 + SO_2 + H_2O.$$

The same year Schroeter[1] published the results he obtained in his repetition of Berthelot's work. Schroeter was interested in the claim that Berthelot had succeeded in obtaining phenol from the products of the reaction of acetylene on fuming sulphuric acid, a synthesis quite remarkable from the fact that Kekule had tried to effect the condensation of an aromatic compound from aldehydes without success. None of the products obtained by Schroeter yielded phenol when fused with caustic potash. Like Muthmam he obtained methionic acid. He also obtained the compound from which methionic acid was supposed to be a decomposition product, acetaldehyde disulphonic acid, $\begin{matrix} CH(SO_2OH)_2 \\ | \\ CHO + H_2O. \end{matrix}$

He obtained among other derivatives its oxime and this fact pointed to the aldehyde formula. There resulted also various sulphates of the above acid with complicated formulas.

Berthelot repeated his work and came to results that confirmed his first conclusions. He obtained the acetaldehyde disulphonate of potassium as in Schroeter's experiment. After the separation of this from the solution, other compounds of the formulas, $C_2H_2\ (SO_4KH)_2$, $(C_2H_2)_3\ (SO_4KH)_4$, were obtained. Examination of these formulas will show that they are of the same empirical composition as

[1] Ber. 31, 2089, and Ann. 303, 114.

those prepared by Muthman and Schroeter. The compound taken by Schroeter for acetaldehyde disulphonic acid, or the supposed intermediate product, $H_3C \cdot CH(O \cdot SO_2OH)_2$, is none other than the acid to whose salt Berthelot gave the formula, $C_2H_2(SO_4KH)_2$. The other product from which he obtained phenol, namely the compound $(C_2H_2)_3(SO_4KH)_4$, may correspond to a mixture of the sulphates of acetaldehyde disulphonic acid found by Schroeter.

With dilute sulphuric acid, composed of three volumes of strong acid and seven volumes of water, different results were obtained by Erdman[1] in 1898. He found that when acetylene was passed into the boiling acid, acetaldehyde was evolved. The formation of the aldehyde was increased in yield by the addition of mercuric oxide, and phosphoric acid gave similar results.

Much of the work described was repeated in this laboratory with acetylene generated from calcium carbide. This repetition was made necessary in order to understand properly the reactions that are to be expected when sulphuric acid is electrolyzed with calcium carbide electrodes in various strengths of acid. It was also necessary to determine the behaviour of calcium carbide towards sulphuric acid of different strengths.

ACETYLENE AND STRONG SULPHURIC ACID.

Acetylene was passed into ordinary strong sulphuric acid without drying the gas. When the color

[1] Zeits. Anal. Chem. 18, (1898), 55.

of the acid had become very dark the product of the absorption was decomposed with water, and an aqueous solution of crotonaldehyde was obtained. Pure monohydrated sulphuric acid also yielded crotonaldehyde. Fuming sulphuric acid, being saturated with acetylene gave no crotonaldehyde. The principal products were the sulphates of acetaldehyde disulphonic acid referred to by Schroeter. These were obtained as a brown horny mass in the case of the barium salts.

ACETYLENE AND DILUTE SULPHURIC ACID.

With sulphuric acid diluted by somewhat more than one half its volume of water, acetaldehyde was obtained when the acid was boiled while acetylene was passed into the flask. The aldehyde was polymerized by means of a small piece of phosphorus pentachloride placed in a Wolff flask connected with the receiver of the distilling apparatus.

When hydrogen was passed together with the acetylene into dilute boiling sulphuric acid containing mercuric oxide in suspension, thioaldehyde was mostly polymerized to trithioaldehyde. It possessed the characteristic alliaceous odor, and was obtained as a cream colored waxy solid.

The operation was performed with a solution consisting of three parts of ordinary concentrated sulphuric acid, and four parts of water. The solution was brought to its boiling point in a flask connected with a condenser and a receiver, while the two gases previously mixed were passed into the acid. The addition of a few grams of mercuric oxide to the

solution, resulted in an increased yield of the thioaldehyde. The mercuric oxide added to the solution was first transformed into sulphate, and this in turn was changed into sulphide, as indicated by its black color. The thioaldehyde solidified in the upper part of the condenser to its polymeric modification, trithioaldehyde. The gaseous products of the reaction, when passed into strong ammonia water, formed a cream colored precipitate mixed with sulphur, and possessed an odor like that of acetamide and mercaptan. Thioaldehyde and free sulphur were also found in the distilling flask.

The formation of the free aldehyde may be accounted for by reason of the catalytic action of the mercury salt on the acetylene. It is not improbable that an intermediate organic mercury compound of acetylene is formed. The reactions may be represented as follows:

$$C_2H_2+H_2S=CH_3CHS,$$

$$3CH_3CHS=S<\begin{matrix}CH(CH_3)S\\CH(CH_3)S\end{matrix}>CH\ CH_3.$$

The thioaldehyde may result by the action of the hydrogen sulphide on the acetaldehyde obtained from the action of the dilute sulphuric acid on acetylene in the presence of mercuric salts.

$$C_2H_2+H_2SO_4\cdot H_2O=H_2SO_4+CH_3CHO,$$

$$CH_3CHO+H_2S=CH_3CHS+H_2O.$$

Thus Weidenbusch[1] found that when hydrogen sul-

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[1] Ann. 66, 158.

phide is passed into an aqueous solution of acetaldehyde, thioaldehyde was obtained.

As I have obtained crotonaldehyde by the action of strong sulphuric acid on acetylene that was generated from calcium carbide, it is evident that the formation of the crotonaldehyde is not due to vinyl haloid impurities, as Zeisel[1] maintained.

In order if possible to throw some light on the action of acetylene on sulphuric acid, some of the derivatives of the latter were treated with acetylene. It was thought that some analogous reaction might be found to explain the varied behaviour of sulphuric acid itself under different circumstances.

NITROSULPHONIC ACID AND ACETYLENE.

Nitrosulphonic acid did not react with acetylene at ordinary temperatures. When the nitrosulphonic acid was dissolved in pure monohydrate sulphuric acid not better results were obtained.

Not only were no signs of reaction observed, but the acetylene failed to react with the sulphuric acid, with which it reacts very readily alone. Moreover the gas after passing through the solution possessed an ethereal odor as if it had been purified from the sulphur compounds that ordinarily give in its alliaceous odor.

CHLORSULPHONIC ACID AND ACETYLENE.

Chlorsulphonic acid was found to absorb acetylene very readily with the evolution of considerable heat. The clear acid became dark-colored. When the

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[1] Ann. 19, 366.

product was poured into water decomposition took place quietly and a black, ill-smelling, viscid mass settled at the bottom of the vessel. Attempts to obtain products pure enough for analysis did not succeed. When the product was distilled a few drops of clear oil were obtained at a temperature of about 100° C., accompanied by decomposition with the separation of carbon and hydrochloric acid. The oil possessed the irritating odor and other characteristics of allyl mustard oil. The oil was decomposed with long continued contact with water. The study of the reaction of acetylene with chlorsulphonic acid is being continued in this laboratory.

REACTION OF ACETYLENE WITH SULPHUR TRIOXIDE.

Regnault,[1] in 1827, found that ethylene united with the vapor of sulphur trioxide, and formed an anhydride of an ethylene sulphonic acid. To the compound was ascribed the formula,

$$\begin{array}{l} CH_2-SO_2-O \\ | \qquad\quad\ \ | \\ CH_2-O-SO_2, \end{array}$$

and it was called carbyl sulphate. With the anhydride it gave rise to ethionic acid,

$$\begin{array}{l} CH_2-SO_2OH \\ | \\ CH_2-O-SO_2OH, \end{array}$$

and when this was boiled with water it broke down into isethionic acid,

$$\begin{array}{l} CH_2-OH \\ | \\ CH_2-SO_2-OH, \end{array}$$

and sulphuric acid.

From the investigation of Schroeter on the action of acetylene with sulphuric acid, it became evident that

[1] Ann. 25, 32.
Pogg. Ann. XLVII, 509.

there is a perfect analogy between the sulphonic acids of ethylene and acetylene. Ethionic acid corresponds to the sulphate of acetaldehyde disulphonic acid, $\begin{array}{l} CH(SO_2OH)_2 \\ \dot{C}H(O\text{-}SO_2OH)_2 \end{array}$. This taking up water gives rise to acetaldehyde disulphonic acid itself.

$$\begin{array}{l} CH(SO_2OH)_2 \\ \dot{C}H(O\text{-}SO_2OH)_2 \end{array} + 2H_2O = 2H_2SO_4 + \begin{array}{l} CH(SO_2OH)_2 \\ \dot{C}H(OH)_2, \end{array}$$

$$\text{or, } \begin{array}{l} CH(SO_2OH)_2 \\ \dot{C}HO \end{array} + H_2O.$$

We should then expect that acetylene on account of the greater chemical activity proper to its unsaturated condition, would also form a compound with sulphuric anhydride analogous to carbyl sulphate. As acetylene has, however, two unsaturated bonds more than ethylene, we may suppose the union of acetylene to take place in two ways:

$$C_2H_2 + 2SO_3 = \begin{array}{l} CH < \begin{array}{l} SO_2 \\ SO_2 \end{array} > O, \\ \dot{C}HO \end{array} \quad \text{or,}$$

$$C_2H_2 + 4SO_3 = \begin{array}{c} O\text{-}O_2S - CH - SO_2 - O \\ O_2\dot{S} - O - \dot{C}H - O - \dot{S}O_2. \end{array}$$

The first of these compounds is the anhydride of acetaldehyde disulphonic acid, the second is the anhydride of the sulphate of acetaldehyde disulphonic acid. Which of these is formed will be seen when examining the decomposition products of the compound with water.

In attempting the union of acetylene with sulphur trioxide, the crystals from a strong solution of fuming acid were used. These were quickly transferred to a retort with a detachable neck. Some phosphorus pentoxide was introduced into the retort with the sulphur trioxide to insure complete dehydration. The neck of the retort was inserted into a receiver cooled with ice. Dry acetylene was passed into the receiver until all the air was driven out of the apparatus, when the sulphur trioxide was distilled from the retort by gently heating the latter.

To insure thorough desiccation the acetylene was passed through a wash-bottle containing sulphuric acid, then through two drying cylinders filled with pieces of calcium carbide and finally, through a long tube of phosphorus pentoxide. The exit tube of the retort, moreover, was connected with a cylinder of fused calcium chloride so that in case air were drawn into the apparatus by reason of the rapid absorption within, no moisture would be admitted.

When the acetylene came in contact with the vapor of sulphur trioxide dense brown-colored fumes appeared in the receiver, and some heat was evolved. The acetylene had to be passed in very slowly to prevent the union from taking place in the neck of the retort, or even in the retort itself.

The product is a yellowish brown substance, at first powdery and apparently amorphous, but soon collecting on the sides of the receiver in ridges that made the glass appear as if corrugated and gilded within. Even under a magnifying power of 60 to 80 diameters no crystalline structure could be made out

with the microscope. The product melted at a moderate heat and simultaneously decomposed with the separation of carbon and the appearance of acid fumes. The compound was extremely deliquescent, and in small quantity melted almost immediately on exposure to moist air and changed to a dark brown syrup. The decomposition product then possessed the faint odor of garlic. Water could not be directly added to the compound, as it decomposed completely with a hissing noise, carbon being separated and sulphuric acid being formed. Sulphur dioxide was also formed when the substance was decomposed with water. The acid of this anhydride was obtained by exposing the compound to moist air for a few days, thus allowing it to absorb water very gradually. In this way the anhydride was not completely broken down by process of decomposition. After the substance had become liquified, water was carefully added and the barium salt obtained by neutralization with barium hydroxide. The excess of the barium sulphate was filtered off and the salt of the acid remained in the solution. No methionic acid was obtained. Acetaldehyde disulphonic acid could not be obtained from the solution by crystallization, nor could the oxime of the same be prepared with hydroxylamine. The solution contained only the barium sulphate of the acetaldehyde disulphonic acid described by Schroeter. He could not obtain it in condition for analysis owing to the variation in composition of the salts. Schroeter gave the acid the formula,

$$\begin{array}{l} CH(SO_2OH)_2 \\ | \\ CH(O\text{–}SO_2OH)_2. \end{array}$$

The barium salt could not be crystallized from the

solution and when heated almost to dryness on a water bath, it solidified on cooling to a hard horny brown mass which could be removed from the dish only with great difficulty. It showed no definite structure, and could not be crystallized from alcohol, or ether, in either of which it did not seem to be appreciably soluble. As no acetaldehyde disulphonic acid or even methionic acid was obtained, but only the sulphate of acetaldehyde disulphonic acid, it was evident from the decomposition of the anhydride into this sulphate, that the formula of the product of the reaction of acetylene on sulphur trioxide is to be represented,

$$\begin{array}{l} O\text{–}O_2S\text{–}CH\text{–}SO_2\text{–}O_2 \\ O_2S - O - CH - O\text{–}SO_2 \end{array}$$

and not as

$$\begin{array}{l} CH < {SO_2 \atop SO_2} > O. \\ CHO \end{array}$$

The reaction of the decomposition of the anhydride like that of the corresponding ethylene carbyl sulphate may be represented as follows:

$$\begin{array}{l} CH_2\text{–}SO_2 - O \\ CH_2 - O - SO_2 \end{array} + HOH = \begin{array}{l} CH_2\text{–}SO_2OH \\ CH_2\text{–}O\text{–}SO_2OH, \end{array}$$

$$\begin{array}{l} O\text{–}O_2S - CH\text{–}SO_2O \\ O_2S - O - CH - O - SO_2 \end{array} + 2HOH =$$

$$\begin{array}{l} HO\text{-}O_2S\text{–}CH\text{–}SO_2OH \\ HO\text{-}O_2S\text{–}O\text{–}CH\text{–}O\text{–}SO_2OH, \end{array} \text{ or, } \begin{array}{l} CH(SO_2OH)_2 \\ CH(O\text{–}SO_2OH)_2. \end{array}$$

All compounds of sulphuric acid and its derivatives that have been discovered in the acetylene series can be shown to be perfectly analogous to the corresponding ethylene compounds. The compound of acety-

lene with sulphur trioxide shows by its decomposition products that it possesses a constitutional formula analogous to ethylene carbyl sulphate. The formation of these compounds is also similar.

$$C_2H_4+2SO_3=\begin{array}{l}CH_2-SO_2-O\\ CH_2-O-SO_2,\end{array}$$

$$C_2H_2+4SO_3=\begin{array}{l}\quad O-O_2S-CH-SO_2-O\\ O_2S-O-CH-O-SO_2.\end{array}$$

Ethylene carbyl sulphate and water gives ethionic acid, and boiled takes up another molecule of water to form isethionic acid and sulphuric acid.[1]

$$\begin{array}{l}CH_2-SO_2-O\\ CH_2-O-SO_2\end{array}+HOH=\begin{array}{l}CH_2-SO_2OH\\ CH_2-O-SO_2OH\end{array}+$$

$$HOH=\begin{array}{l}CH_2SO_2\ OH\\ CH_2OH_2\end{array}+H_2SO_4,$$

$$\begin{array}{l}O_2S-O-CH-O-SO_2\\ \ O-O_2S-CH-SO_2-O\end{array}+2HOH=\begin{array}{l}CH(SO_2OH)_2\\ CH_2(O-SO_2OH)_2\end{array}+$$

$$2HOH=\begin{array}{l}CH(SO_2OH)_2\\ CH(OH)_2,\end{array}\text{ or, }\begin{array}{l}CH(SO_2OH)_2\\ CHO+HOH\end{array}$$

The reactions with acetylene and sulphuric acid derivatives are more complicated than those of ethylene as there are two additional valencies to be satisfied. As a consequence of loading down the molecule decomposition into simpler derivatives is to be expected whenever it seems possible to separate the stabler elements of water and sulphuric acid. As is

[1] Pogg. Ann. 47, 509.

seen by comparing the foregoing reactions, corresponding to ethionic acid we have in the acetylene series the acid, $\begin{matrix} CH(SO_2OH)_2 \\ \dot{C}H(O\text{–}SO_2OH)_2, \end{matrix}$ which is mentioned by Schroeter[1]. Acetaldehyde disulphonic acid, the decomposition product, is the acid corresponding to isethionic acid. It may be likely that the formula of Muthman, $\begin{matrix} CH(SO_2OH)_2 \\ \dot{C}H(OH)_2, \end{matrix}$ may be applied to it as it does not give up water even when attempts were made to crystallize its salts over phosphorus pentoxide. Its salts of monovalent metals contain one molecule of water and its salts of bivalent bases contain two molecules of water which can not be separated without complete decomposition of the compound. The formula of Schroeter also has reasons for its application because of the property of the acid to form an oxime and other derivatives characteristic of aldehydes. As a further decomposition product of both isethionic acid and acetaldehyde disulphonic acid we finally have methionic acid.

Ethylene when passed into fuming sulphuric acid yields isethionic[2] acid directly, and acetylene under the same conditions gives acetaldehyde disulphonic acid.

When ordinary strong sulphuric acid or an acid more or less hydrated is used, none of the compounds above mentioned is formed in appreciable quantity. There is nevertheless reason to believe that here also

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[1] Ann. 303, 114.
[2] Pogg. Ann. XLVII, 509.

the analogy of the formation of the analogous compounds still holds true.

Faraday,[1] Hennel, Regnault and Magnus tried the action of ethylene on sulphuric acid or its anhydride. Hennel found that when ethylene is led into sulphuric acid ethyl sulphuric acid is formed. Berthelot repeated the work of Hennel and obtained the same results, namely ethyl sulphuric acid and alcohol.

When ordinary sulphuric acid is used the product differs completely from that obtained by the action of ethylene on an acid containing free sulphur trioxide, as may be seen by comparing the formulas of the compounds in question. Ordinary sulphuric acid with ethylene gives ethyl sulphuric acid, a metamer of isethionic acid.

Sulphuric Acid. Ethyl Sulphuric Acid.

$$\begin{matrix} HO \\ HO \end{matrix} > SO_2, \qquad \begin{matrix} (C_2H_5)O \\ HO \end{matrix} > SO_2,$$

Isethionic Acid.

$$\begin{matrix} C_2H_4(OH) \\ HO \end{matrix} > SO_2.$$

Ethyl sulphuric acid, the product of the action of ethylene on strong sulphuric acid gives alcohol or ether when distilled, according to the conditions of the experiment.

$$\begin{matrix} CH_2 \\ \ddot{C}H_2 \end{matrix} + \begin{matrix} HO \\ HO \end{matrix} > SO_2 = \begin{matrix} (C_2H_5)O \\ HO \end{matrix} > SO_2.$$

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[1] Philosophical Transactions, (1826) 240, (1828) 365. Ann. Chim. Phys. XXX., 154, (1827). See also Moniteur Scientifique, 4 Ser. XVIII., p. 7, 15, 21.

$$\frac{(C_2H_5)O}{HO}>SO_2 + HOH = C_2H_5OH + \frac{HO}{HO}>SO_2$$

$$\frac{(C_2H_5)O}{HO}>SO_2 + C_2H_5OH = \frac{C_2H_5}{C_2H_5}>O + \frac{HO}{HO}>SO_2$$

Berthelot tried to obtain the alcohol of the acetylene series, vinyl alcohol. It was shown that the principal, if not the only product of the action of acetylene on sulphuric acid, is crotonaldehyde. The crotonaldehyde is the result of the condensation of two acetaldehyde residues. Though a number of attempts have been made to isolate vinyl alcohol[1] at different times, success has not as yet been met with. As a matter of fact all reactions in which the compound is to be expected from its well known derivatives, not vinyl alcohol but acetaldehyde is obtained. Thus, for example, Semmler[2] expected to obtain vinyl alcohol from divinyl sulphide treated with silver hydroxide, but acetaldehyde resulted instead.

$$\frac{CH_2:CH}{CH_2:CH}>S + Ag_2(OH)_2 = Ag_2S + 2CH_3CHO.$$

It seems that all the reactions looking to the formation of vinyl alcohol really give acetaldehyde. Rearrangement of the molecule takes place at the moment of the reaction. If vinyl alcohol is really the product formed when acetylene acts on sulphuric acid, dilution of the acid is sufficient both to break

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[1] Ann. Chim. Phys. (3), LXVII, 6, (1863). Ann. Chim. Phys. (7), XVII, 29, 7, (1869). Ber. 22, 2863. Gaz. XXIX, (1), 390.

[2] Ann. 241, 113.

up the compound and condense the acetaldehyde to crotonaldehyde. How then are we to explain the formation of the acetaldehyde and crotonaldehyde from the point of view that the reactions of ethylene and sulphuric acid derivatives and acetylene and its derivatives are analogous?

The fact is that, whether vinyl sulphuric acid be present in the action of acetylene on dilute or ordinary concentrated acid, or some other compound be formed, acetaldehyde or crotonaldehyde is obtained as the final product. It has been generally supposed that acetaldehyde simply takes up the elements of water, but this is no explanation, and is in fact hardly likely. Acetylene and water do not unite except in the presence of some catalytic agent, such as mercury salts, carbon or sulphuric acid. Two methods of explanation present themselves. According to one of these we may suppose the presence of vinyl sulphuric acid, as Berthelot maintains, according to the reaction:

$$C_2H_2 + {HO \atop HO} > SO_2 = {(CH_2:CH)O \atop HO} > SO_2,$$

$${(CH_2:CH)O \atop HO} > SO_2 + HOH = (CH_2:CHOH) + {HO \atop HO} > SO_2,$$

$$(CH_2:CHOH) = CH_3CHO.$$

As vinyl alcohol can not exist as such, it undergoes rearrangement of its molecule and acetaldehyde is evolved in dilute solutions of acid. If the acid is

strong the acetaldehyde is simultaneously polymerized to crotonaldehyde:

$$CH_3CH\ O\ + \\ CH\ H_2\ CHO = CH_3CH:CH\ CHO + H_2O.$$

Whatever the nature of the hydration of acetylene it is evident that warm diluted sulphuric acid performs a sort of a catalytic action in the production of aldehyde not unlike the action of aluminium chloride in the chlorination of hydrocarbons. At low temperatures the definite compound of sulphuric acid and water separates in crystals of the composition, $H_2SO_4.HOH$, which melt at 10.5° C. It may also be likely that this definite compound gives up the hydrogen and the hydroxyl group to acetylene and then takes up another molecule of water. When the acid becomes of a certain dilution acetaldehyde ceases to be formed, and this fact would strengthen the theory. When the acid contains little or no water the elements of water are abstracted from two molecules of acetaldehyde, and one molecule of crotonaldehyde results. The reactions may be represented as follows:

$$C_2H_2 + H_2SO_4 \cdot H_2O = CH_2:CHOH + H_2SO_4,$$

$$CH_2:CHOH = CH_3CHO,$$

$$H_2SO_4 + H_2O = H_2SO_4 \cdot H_2O.$$

In case no water be present we would have the reaction:

$$CH_3\ {}^{CH\ O}_{CH\ H_2}\ CHO + H_2SO_4 = CH_3CH:CH \cdot CHO + \\ H_2SO_4 \cdot H_2O.$$

Pure monohydrate sulphuric acid reacts with acetylene like ordinary concentrated sulphuric acid, and the product on dilution gives crotonaldehyde as the principal product.

Other substances besides sulphuric acid possess the power of acting as catalytic agents in oxydizing or hydrating acetylene. Degrez[1] found that acetylene is absorbed by carbon, and when this was heated with water in closed tubes, acetaldehyde was obtained. The salts of mercury produce the same result when boiled in aqueous solution while a stream of acetylene was passed into them. The yield of acetaldehyde seems to be increased in the presence of free acid. In the last case the evolution of the aldehyde is due to the formation and subsequent decomposition of vinyl or aldehyde derivatives containing mercury, as will be shown more fully in another paper. These mercury derivatives are the intermediate products. Some have already been isolated and their formulas determined with accuracy, others will be described in a special article further on.

FORMATION OF ALDEHYDE FROM ACETYLENE IN PRESENCE OF FINELY DIVIDED PLATINUM.

Finely divided platinum may also be used to cause acetylene to take up the elements of water. When acetylene is passed for some time into reduced platinum suspended in water acidified with dilute nitric acid, aldehyde is formed. The product is allowed to stand by itself for some time in order to permit all the acetylene in solution to change into aldehyde.

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[1] Bull. Soc, Ch. XI, 362.

The odor of the gas disappears and that of acetaldehyde becomes very noticeable. The product is filtered and the filtrate treated with iodine and caustic potash to an alkaline reaction when an abundant precipitate of iodoform is obtained. When the suspended platinum is acidified with hydrochloric acid no aldehyde is obtained. Similar results could not be obtained in alkaline solutions in which reduced cobalt was suspended.

Acetylene shows the general tendency to form aldehyde derivatives and behaves like acetaldehyde itself in many reactions. Towards sulphuric acid the action of acetylene and acetaldehyde is exactly similar. Weidenbusch[1] first noticed that acetaldehyde was absorbed by sulphuric acid, but he threw no light on the nature of the reaction that takes place. He simply stated that the acid became dark-colored when aldehyde was passed through it.

Delepine[2] found that ordinary aldehyde gave definite products with strong sulphuric acid. The latter yielded as a product of reaction the same compounds as were obtained by Schroeter by the action of acetylene on the acid under the same conditions. Acetaldehyde disulphonic acid and methionic acid were obtained. With ordinary strong sulphuric acid crotonaldehyde resulted on dilution of the product, as Kekule had found before. This is likewise the product obtained from the action of acetylene upon sulphuric acid as Lagermarck and Eltekow, and

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[1] Ann. 66, 155.

[2] Compt. Rend. 133, 875.

Zeisel have shown. Other derivatives of acetaldehyde, such as acetamide and chloral also give rise to acetaldehyde disulphonic acid when treated with fuming sulphuric acid. In summing up the results we may conclude that the analogy of the reactions between acetylene and ethylene in their behaviour towards sulphuric acid generally holds true.

1.—Acetylene in dilute boiling solutions of sulphuric acid is oxydized to vinyl alcohol and this by intramolecular rearrangement becomes acetaldehyde. It is probable that a vinyl compound is first formed which being very unstable breaks down into the other compounds just mentioned.

2.—In the presence of strong sulphuric the acetaldehyde supposed to be formed is condensed to crotonaldehyde with the separation of water; ordinary alcohol heated with concentrated sulphuric acid also loses water and is changed to ether.

3.—With fuming sulphuric acid the derivatives of acetylene are perfectly analogous to those of ethylene, being the sulphonic acids of ethylene and acetylene as already mentioned.

4.—Sulphur trioxide gives an anhydride with acetylene similar to the ethylene compound. It decomposes with the addition of water into the sulphate of acetaldehyde disulphonic acid, which is analogous to ethionic acid in the ethylene series. Further decomposition changes this sulphate into acetaldehyde disulphonic acid which is analogous to isethionic acid the compound similarily obtained from ethionic acid.

THE ACTION OF SULPHURIC ACID ON CALCIUM CARBIDE

The behaviour of sulphuric acid toward calcium carbide varies according to the conditions under which the experiment is carried on, such as temperature of the operation, the strength of the acid used, and the degree of fineness of the calcium carbide employed. Dilute sulphuric acid differs little in its action on carbide from water. The water present decomposes the carbide and calcium sulphate results by the further action of the acid.

1.—Whenever the action of a compound with calcium carbide is very rapid much heat is given off by reason of the endothermic nature of the compound and very often total decomposition takes place. When concentrated sulphuric acid is allowed to drop on pieces of calcium carbide the size of a pea, or when powdered carbide be thrown into strong sulphuric acid this total decomposition takes place without the application of external heat. In general when finely divided carbide is used the breaking down of the acid and the separation of carbon can only be prevented by cooling the acid in a freezing mixture or throwing pieces of ice into the acid.

In an experiment performed a flask of five litres capacity was used and a mixture of about one hundred grams of granulated and powdered calcium carbide was put into it. From a dropping funnel strong sulphuric acid was allowed to fall upon the mixture. The first drop caused a strong evolution of vapors, the violence of the reaction increasing as more heat was evolved. The gases

were passed through a well cooled receiver. The mass of the carbide became brown, and finally much carbon separated. Sulphur dioxide, hydrogen sulphide, acetylene and carbon dioxide were given off. By far the greater portion of the gas consisted of sulphur dioxide and acetylene. Hydrogen sulphide was present in great quantity, especially at the beginning of the operation and later on it ceased to be formed. Lead acetate gave at first a black precipitate of the sulphide but later only the sulphite was obtained. The acetylene was determined by absorption with silver nitrate in ammoniacal solution. The residue in the flask consisted of a dirty black mass composed principally of calcium and magnesium sulphates and carbon. When the decomposition was carried on while heating the acid in the flask and allowing calcium carbide slowly to fall into the acid the action was more violent but no different results were obtained.

2.— Powdered and granulated carbide was added to strong sulphuric acid cooled in ice-water. Decomposition took place slowly and the action could not be well regulated. Acetylene was evolved with some hydrogen sulphide, sulphur dioxide came off when the action became uncontrollable. Constant stirring was necessary to prevent this complete decomposition with the evolution of sulphur dioxide. The mass did not become brown but calcium sulphate was precipitated and the mixture became a pasty consistency. The odor of hydrogen sulphide was only noticed after standing for some days. Neither aldehyde or crotonaldehyde could be noticed. The characteristic odor

of thioaldehyde was present when the mixture was diluted.

3.—When acid more dilute was used, for example, of specific gravity 1.75, or when strong acid was allowed to stand uncovered so that moisture could be absorbed from the atmosphere, a precipitate soon occurred, decomposition took place slowly, and hydrogen sulphide was evolved with the acetylene. After a few days the strong odor of thioaldehyde was noticed. The thick emulsion was somewhat diluted with water, put into a large flask and carefully heated to the boiling point. The distillate contained not even traces of either acetaldehyde or crotonaldehyde. The thioaldehyde heated in an acid solution was polymerized to parathioaldehyde which was precipitated as a yellow waxen mass in the cooler parts of the condenser. The thioaldehyde was supposed to result either from the action of the nascent acetylene on hydrogen sulphide, or from the action of hydrogen sulphide on ordinary aldehyde. A mixture of iron sulphide and carbide gave an increased yield of the thioaldehyde when treated with acid of the same concentration.

In the experiments just described the solution was carefully examined for organic salts. Only the faintest traces of formic acid were found. Magnesium sulphate was found in quantity, neither acetaldehyde disulphonic acid or methionic acid could be detected in their salts, nor any of the compounds mentioned by Schroeter. To make sure that none of these products if present might escape observation, the calcium salts of the filtrate were changed into the barium zinc and other metallic compounds but

no organic substances were found in appreciable quantity, though large amounts of material were repeatedly employed. The magnesium sulphate was mixed with some tarry impurities when evaporated to dryness but even here only traces of organic matter were shown by ignition. Repetitions of these attempts gave the same results; a trace of formic acid and parathioaldehyde.

4. —The action of calcium carbide on stronger acid of specific gravity 1.82 to 1.84 gave by slow action quite different results at ordinary temperatures. Four or five liters of this acid were poured into a beaker and several large pieces of calcium carbide were immersed in the acid so as to be completely covered. The beaker was placed in a stronger vessel to guard against the evil results of breakage, and was carefully covered to prevent the absorption of water from the atmosphere. The action was very slow, and in winter weather would continue a month before evident results could be obtained from a test-portion diluted with water. In the summer and in direct sunlight a few days were sufficient to bring out decided results and the acid began to take on a chocolate color. At first the carbide steadily gave off small bubbles, and a faint sweet smell mixed with the odor of sulphur dioxide was evolved. For some time the calcium carbide presented a clean surface to the acid as the calcium sulphate was dissolved to a clear solution. On the whole the evolution of gas was extremely slow. After a while the excess of sulphate could no longer be held in solution and the acid became viscid and muddy. During the process the

solution was frequently stirred, yet care had to be taken not to move about the pieces of carbide too violently as a series of surface explosions occurred when the carbide was rubbed gently with a glass rod These small detonations were like the explosion of a percussion cap and were accompanied with the appearance of a flash of bright light. A gas was given off which on coming in contact with the air gave a small cloud of smoke. When the carbide was moved over the bottom of the vessel a continuous rattle of these minute explosions was obtained and the flash of flame was at times two centimeters in length. This phenomenon occurred as long as the surface of the carbide was kept from the sediment of calcium sulphate. The explosions did not occur on the whole surface of the carbide, but principally at metallic looking nodules. Sharp edges gave the explosions very energetically. The phenomenon might be due to minute pieces of free calcium, to calcium phosphide giving off phosphine, or to silicon compounds giving off silicon hydride. The explosions never occurred unless the carbide was rubbed or moved. They have not been known to take place spontaneously.

When the pasty mass, the product of the experiment just referred to, was poured into cold water, the strong odor of crotonaldehyde was given off and calcium sulphate was immediately precipitated. Upon subjecting the decomposed mixture to distillation, vapors passed over with some water at a temperature below 100° C. The distillate possessed the odor and the other characteristics of crotonaldehyde as described

by Kekule[1]. The crotonaldehyde was oxydized to crotonic acid by means of silver hydroxide. A bright silver mirror was obtained acccording to the reaction:

$$2CH_3CH:CHCHO+3Ag_2O=$$
$$2CH_3CH:CHCOOAg+H_2O+4Ag.$$

After filtering off the excess of the silver oxide, the solution was heated on a hot water bath to obtain the silver salt, but decomposition set in. The vapors evolved possessed a rancid odor and a dark-colored precipitate was left in rings on the dish as the water evaporated. As the silver salt could not be obtained it was changed into the barium salt with barium carbonate. The barium salt crystallized from water in small cubes.

Part of the distillate was treated with sodium carbonate and iodine and on warming an abundant precipitate of iodoform was obtained. The crystals were filtered and their melting point found to be 119° C. The product was pure iodoform. Reduction with zinc dust gave the nauseating odor of butyric alcohol.

5. — Monohydrated sulphuric acid was also treated with calcium carbide in the same manner as described for sulphuric acid. The action was more rapid, and cooling had to be applied to prevent complete decomposition of the acid. In a few hours the action was almost completed. The acid became so pasty that the contents could not be poured from the vessel. Similar results were obtained as in the preceding experiment, but the yield of crotonaldehyde

[1] Ann. 162, et Seq.

was much better in proportion to the amount of the acid used.

ELECTROLYSIS OF VARIOUS SOLUTIONS WITH CALCIUM CARBIDE ELECTRODES.

Before entering upon the course of experiments, I shall detail some of the methods used in the analysis of the gaseous products, as most attention was paid to the volatile products that were formed. Considerable difficulty was experienced in the separation and analysis of the gases formed. Though it is easy to obtain absorbents for the individual gases, their complete elimination and separation is in some cases a very tedious operation, and often the separation volumetrically was found to be impossible.

Ammoniacal cuprous chloride has been used as an absorbent for acetylene, but as it dissolves indefinite amounts of ethylene according to the concentration of the solution of the absorbent, it can not be used without modification of the method. The separation of acetylene from sulphur gases is very difficult volumetrically. No absorbent has been found that will perfectly and quickly separate sulphur gases without affecting the ethylene and acetylene present. The method of Berge and Reychler[1] for the purification of the acetylene though it may remove all phosphine, nevertheless dissolves large amounts of the hydrocarbon with the formation of definite mercury compounds. The authors claim that the solution can be used for quantitative separation of the gases, and

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[1] Bull. Soc. Chim. III, XVII, 218, (1897).

recommend a solution consisting of eighty parts of water, twenty of hydrochloric acid and eight of mercuric chloride. The gas is first passed through caustic potash, where the sulphur gases and carbon dioxide are removed. Hydrogen sulphide is changed to sulphate in the potash solution. Phosphorus is changed to phosphate and determined gravimetrically by the method of Sonnenschein. I have tested the purifying agent of Berge and Reychler to see if it could be used volumetrically, but negative results were obtained. In the first place hydrogen sulphide is not perfectly absorbed by caustic potash as was found by test experiments on known volumes of gases. Moreover, the potash solution holds acetylene gas in solution in varying proportions according to the concentration. If the caustic solution be previously saturated with acetylene the difficulty is not overcome. Unreliable variations occur. Lead acetate will take up all the hydrogen sulphide, but acetylene is also absorbed, and the quantities taken up vary.

Although the absorbent of Berge and Reychler does not precipitate acetylene the gas is nevertheless dissolved with the formation of definite compounds, as was shown by Biginelli.[1] I have found that ninety-five per cent. of the gas is taken up by the reagent. It can not then be used in the Hempel absorption apparatus. If the solution be previously saturated with the gas, the absorbent can not be relied on as it gives erratic results. It has accordingly been found

[1] Ann. di Farm. e Chim. (1898), 16. Cent. (1898), 925.

necessary to omit the elimination of the phosphine. At all events the traces are quite faint and would not tend to influence the results of the experiments appreciably.

The various constituents of the gaseous product were successively taken out by their proper absorbents and the apparatus used for the analysis was of the type introduced by Hempel For the elimination of the acetylene, however, the Bunte-Seger apparatus was used in connection with the Hempel burettes and pipettes.

The substances liable to be met with in this work are somewhat limited and consist principally of acetylene, ethylene, ethane, oxygen, carbon dioxide and carbon monoxide, traces of sulphur dioxide and hydrogen sulphide. Ammonia and oxides of nitrogen are to be met with. Sulphur dioxide was generally found in such small quantities as to be negligible. The gas mixture was in every case left to stand over water for some time in order to allow gases soluble in water to be taken out. Acetylene was in every instance taken out first because of the quantity present and because it is taken in solution by nearly all of the other absorbents in greater or less degree. The absorption was made by the method described by Moody and Tucker.[2] The authors found that an ammoniacal solution of silver salt is the best absorbent for separating acetylene from ethylene volumetrically. To a solution of silver nitrate hydrochloric acid is added until an acid reaction is obtained.

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[2] Jour. Amer. Chem. Soc. 23, 671.

Ammonia water is then added until the reaction is just alkaline. This was found to be a better solution than ammonical cuprous chloride which absorbs large quantities of ethylene. The gas can be regained, however, on boiling the cuprous chloride solution as Berthelot[1] described but the method is longer and more tedious. I have examined Moody and Tucker's reagent with known mixtures of the two gases. Though it is not as sensitive to small quantities of acetylene as ammoniacal cuprous chloride, and though the last traces of the gas can be eliminated only after a long absorption, the use of the Bunte-Seger apparatus effects the completion of the operation in a very short time.

The ethylene is separated in the usual manner over fuming sulphuric acid containing crystals of sulphur trioxide. Hydrogen was taken out by means of palladium as described in the manuals of gas analysis. The ethane was determined by explosion after the hydrogen had been removed. It was also calculated by silent combustion in a Winckler's pipette with incandescent platinum spiral. Of the anode products carbon dioxide was quickly removed in the caustic potash pipette. Acetylene was next taken out and then oxygen with the phosphorus pipette.

ELECTROLYSIS OF SULPHURIC ACID WITH CALCIUM CARBIDE ELECTRODES.

(PRELIMINARY EXPERIMENT.)

Before the operation described by Harris[2] had come

[1] Ann. Chim. Phys. 3, LXVII, 57, (1863).

[2] Electrochemical Industry, p. 131, (Vol. 1.) No. 4, (Dec. 1902).

to my notice experiments somewhat similar had already been made in this laboratory. The object of the work was to effect results such as those mentioned by the author, namely to obtain alcohol or ether from acetylene by means of electrolysis. Instead, however, of passing acetylene into heated sulphuric acid, one or two soluble electrodes of calcium carbide were used. At the carbide cathode the hydrogen ions would come in contact with nascent acetylene slowly given off by the electrode which reacted with the acid or rather with the water in the sulphuric acid. The first experiment was conducted with no other end than to obtain qualitative results. It was expected that the ethylene uniting with the sulphuric acid would form ethyl sulphuric acid and that ether or alcohol would be obtained from this on diluting or distilling the product. The distillate gave the iodoform test unmistakably, in fact it was possible to obtain considerable quantities of the latter compound. To be sure that the iodoform was really due to alcohol, the experiments already referred to, or the action of acetylene on sulphuric acid, were undertaken. It was found that iodoform was obtained even when no current had been used, both when acetylene was allowed to act on sulphuric acid, and when calcium carbide was allowed to react with stronger sulphuric acid. As, however, the iodoform test does not prove conclusively the presence of alcohol, it will be necessary to obtain and analyze alcohol as such. If the ethylene which is present previous to the formation of ethyl sulphuric acid, be collected and analyzed, we may conclude that the iodoform test was obtained at

least partly from the alcohol that was formed.

Principally the gaseous products of the experiments will be examined in order to arrive at definite conclusions as to the presence of alohol. I shall now describe some of the experiments performed in the electrolysis of sulphuric acid with calcium carbide electrodes.

In the preliminary experiments the apparatus used is represented in figure (1). A well-shaped piece of calcium carbide was chosen for each electrode. A hole about one half a centimeter in diameter was bored into one end with a steel drill, and a copper wire was fastened into this with melted lead. The electrodes were contained in porous cups in order to examine separately the products of reaction at each pole. Each porous cup was closed with a stopper through which a Wurtz tube was passed. The electrical connections with the poles were made through the corks of the Wurtz tubes, while the gas was conducted through the side tubes into separate gasometers. The electrodes dipped only partly below the surface of the acid in each cup, and the operation of electrolysis was carried on in a large thick walled vessel. The thermometer in the vessel registered the temperature during the experiment.

In dilute solutions of sulphuric acid acetaldehyde is present at least when heated. At the anode simultaneously with the oxidation of acetylene to carbon dioxide and water, aldehydes might become acids. At the cathode, reduction of aldehyde would take place to form alcohol. Acetylene might likewise be changed to ethylene with the subsequent formation

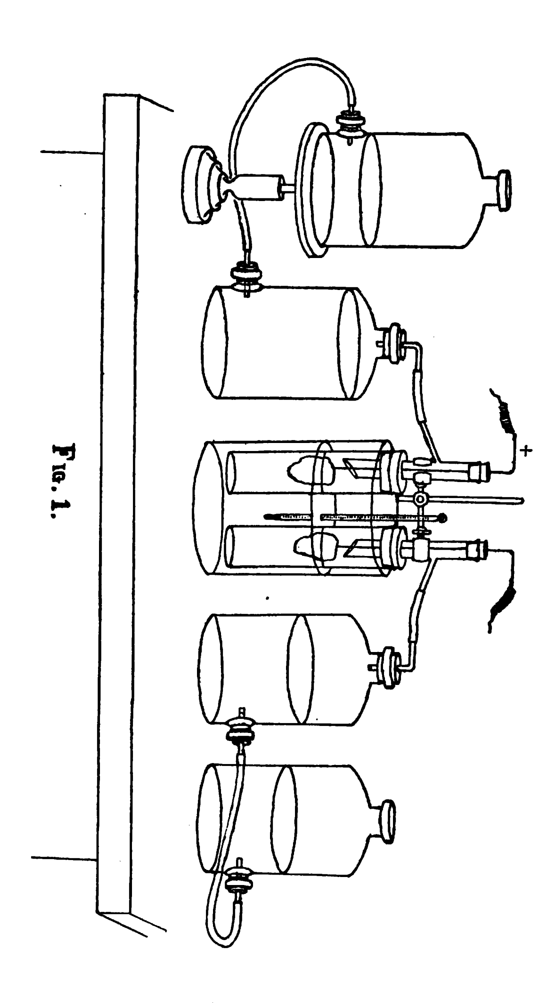


Fig. 1.

of ethyl sulphuric acid. It remains then to be found out whether the actual results in the experiments to be described correspond to the expectations entertained in regard to the formation of the compounds enumerated.

Calcium carbide has been found to conduct electricity to a considerable extent, though compared to the metals it has a low conductivity. This great resistance to the current is one of the principal difficulties to be contended with in using this substance as an electrode. Owing to the great electromotive force that must be used, the calcium carbide becomes very much heated. If the contact is not very good the copper wires at this point are often melted.

In cold concentrated aqueous solutions of some salts, calcium carbide is very stable. Concentrated sulphuric acid attacks it very slowly, and it is generally necessary to add water in order to increase the evolution of gas. Concentrated calcium chloride and calcium nitrate solution are almost without any action upon calcium carbide, and must in neutral solution be diluted with even more water than sulphuric acid. Zinc chloride and sodium hyposulphite must also be diluted when concentrated solutions are used. It was thought advisable to use these solutions of salts in order to obtain decisive results as to the presence of ethylene, in the electrolysis of electrolytes with calcium carbide cathode.

I have already referred to electrolysis in the presence of acetylene gas in solution in the electrolyte. I have not been able to find that any attempt was made to use calcium carbide as a soluble electrode

giving off nascent acetylene. We should expect that if an electrolytic synthesis were likely to take place it ought to occur where the constituents are present in the nascent state. If hydrogen unites to acetylene to form ethylene, as Wilde and Berthelot have shown, we should expect the same result at the cathode of calcium carbide. The ethylene thus formed in sulphuric acid solution would unite with the acid to form ethyl sulphuric acid. This at the proper temperature would give off ether and alcohol according to the conditions of dilution or concentration. It would be simply necessary to maintain in the solution of acid the proper proportion of water. The action was expected to take place as follows:

$$CaC_2 + H_2SO_4 \cdot H_2O = CaSO_4 + C_2H_2 + H_2O,$$

$$H_2SO_4 = 2\overset{+}{H} + \overset{\mp}{SO_4}, \text{ or } \overset{+}{H} + \overset{\mp}{HSO_4},$$

$$C_2H_2 + 2\overset{-}{H} = C_2H_4,$$

$$C_2H_4 + H_2SO_4 = \begin{matrix} C_2H_5O \\ HO \end{matrix} > SO_2,$$

$$\begin{matrix} C_2H_5O \\ HO \end{matrix} > SO_2 + H_2O = C_2H_5OH + H_2SO_4,$$

$$\begin{matrix} C_2H_5O \\ HO \end{matrix} > SO_2 + C_2H_5OH = (C_2H_5)_2O + H_2SO_4.$$

During the subsequent experiments the current used in the electrolysis was obtained from a storage battery of fifty cells. A voltmeter and ampèremeter registered accurately the constants of the current. For the experiment in question an electromotive force

of one hundred volts was used. The electrolyte was ordinary concentrated sulphuric acid somewhat diluted during the experiment in order to obtain a suitable flow of gas before turning on the current. On turning on the switch an immediate increase of the flow of gas was noted. After the operation had been allowed to continue for some time to drive the air out of the apparatus, and also to obtain normal conditions of experiment, the gas was collected in separate gasometers from both poles simultaneously. The reaction was continued for more than three hours, during which a considerable rise of temperature occurred, and the acid began to take on a brown color both in the cups and in the solution outside of the cups. The average temperature was noted at different stages of the operation. The greatest rise was noted in the path of the current, being about 70° to 71° C.

Sulphur dioxide was given off in small quantity as the acid was decomposed. This occurred principally at the cathode where the reduction takes place. After the experiment the cathode was found to be very little changed, though covered with a dark slimy sediment. The anode was blackened and eaten away, as if the acetylene had been completely decomposed with the separation of carbon. After standing for some time the contents of the porous cups were separately analyzed, and the gases from the separate poles were examined. Of the 56.6 ccm. of the gas obtained at the anode only 7 ccm. were found to be acetylene. No ethylene resulted. No trace of alcohol or ether was found. On decomposing the con-

tents of the porous cups with water an ethereal odor was noticed, and when the product was distilled a volatile compound passed over with water vapor before the thermometer registered 100° C. The distillate possessed the odor of crotonaldehyde, and gave a voluminous precipitate of iodoform with sodium carbonate and iodine. The product showed all the characteristics of crotonaldehyde. It was oxidized to crotonic acid by freshly precipitated silver oxide. A salt was obtained that could not be evaporated on the water bath without decomposition. During the breaking down of the compound the fumes given off possessed the rancid odor of butyric acid. The iodoform obtained was filtered, dried and purified by crystallization. It melted at 119° C. exactly. Considering the small amount of acid decomposed the yield of iodoform was considerable. The mirror test for aldehyde was also obtained. It would be inconclusive to maintain that the iodoform test was due to the presence of alcohol since the product of distillation gave an aldehyde reaction and possessed none of the other characteristics of ethyl alcohol. Moreover as Lieben has shown aldehydes give the iodoform reaction far more readily than ethyl alcohol. As the gaseous product gave no trace of ethylene it seemed evident that the current might not have effected the union of nascent hydrogen with nascent acetylene. In order to establish with certainty whether acetylene could be united with nascent hydrogen at the cathode of calcium carbide an extended series of experiments was undertaken with various electrolytes with which ethylene does not form a compound. If the product

of the electrolysis of dissolved acetylene in sulphuric acid solutions be really alcohol then by using an electrolyte that does not absorb ethylene the gas can be estimated volumetrically by the methods of gas analysis.

ELECTROLYSIS OF DILUTE SULPHURIC ACID WITH CALCIUM CARBIDE ELECTRODES.

As dilute sulphuric acid does not readily absorb ethylene attempts were made to obtain the free gas by electrolyzing the dilute acid. In performing the operation some difficulty was experienced. When the acid was too dilute the carbide was rapidly eaten away and a layer of calcium sulphate was formed on the surface of the electrode. This acted as an insulator or retarded the passage of the current. When on the contrary the acid was too strong little or no acetylene was given off. Water was constantly being used up to cause a steady evolution of acetylene, and accordingly it was difficult to keep a constant concentration of acid.

The apparatus used in this experiment is represented in figure (2). The electrolyte was a ten per cent. solution of ordinary concentrated sulphuric acid. The specific gravity of the acid at the beginning of the operation was 1.09 at 33° C. An ordinary thick-walled gas-cylinder was used as an electrolyzing vessel. Contact at the cathode of calcium carbide was made by means of a mercury connection. A bent glass tube within which was a copper wire served to connect the mercury at the bottom of the vessel with the battery. The chloroform was gently poured upon

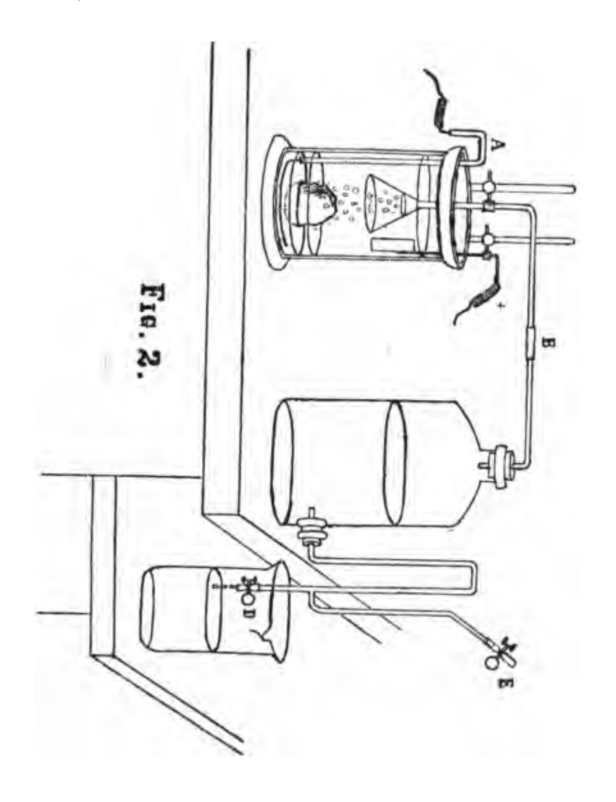


Fig. 2.

the mercury to the height of several centimeters, and served to insulate the mercury from the electrolyte. A shapely piece of calcium carbide was then floated upon the mercury so as to present a large surface to the electrolyte. The acid was the introduced and the electrolysis was begun, using a platinum anode. The gasometer was filled with water to the connection (B). The siphon (D) was also completely filled with water. A funnel connection with a tube bent at right angles, was placed so as to connect all the evolved gases, and after the current had passed for some time to allow the air to be driven from the funnel, the connection was made at (B) and the gases drawn into the gasometer by regulating the overflow of water from the siphon at (D). Without much careful manipulation the gas could be collected as fast as it was given off. When sufficient gas has been collected at the cathode of carbide the operation was interrupted and the products analyzed.

The conditions of the experiment are given below.

TEMPERATURE.	CURRENT.	TOTAL GAS EXAMINED.	ACETYLENE FOUND.	ETHYLENE FOUND.	RESIDUE.
I.—21° C.	2.25 Amp.	95. ccm.	25.8 ccm. 28 per ct.	3.2 ccm. 3 per ct.	64. ccm. 68.5 per ct

SECOND SERIES OF EXPERIMENTS WITH DILUTE SULPHURIC ACID.

A solution containing equal parts of strong sulphuric acid of the specific gravify 11.83, and of water, was electrolyzed in an apparatus as shown in figure (3). The specific gravity of the diluted acid used as an electrolyte was 1.479 at 40° C.

A calcium carbide cathode was used. A piece of

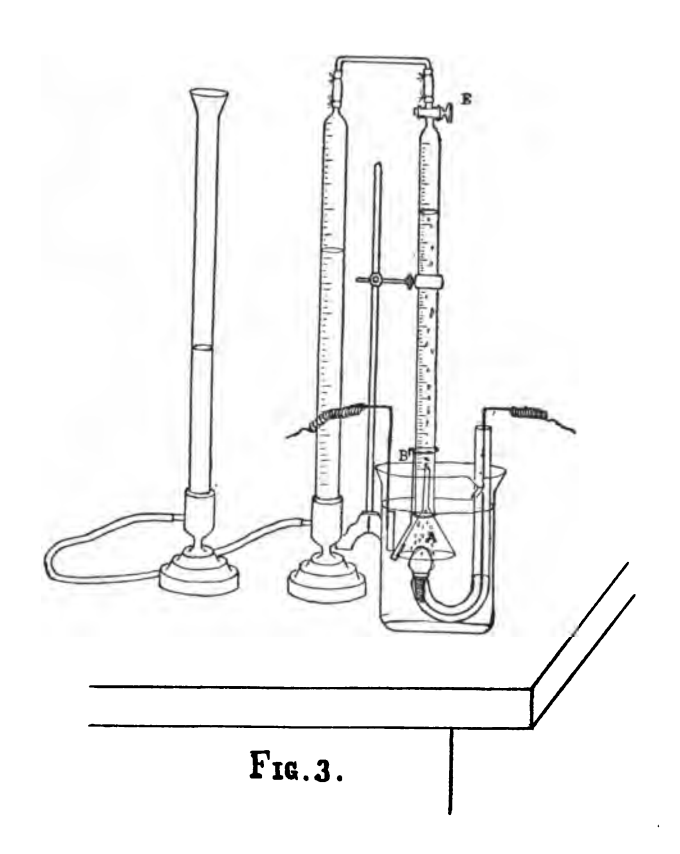


Fig. 3.

calcium carbide was shaped as shown in the illustration, having a large head and a cylindrical projection. Many coils of fine copper wire were wound around the cylindrical end, thus connecting it with a larger copper wire bent like a fish-hook. A piece of thick rubber tubing served to insulate the copper wires from the solution so that the electrical connection with the electrolyte was obtained only at the globular end of the calcium carbide electrode. Mercury was poured into the rubber tube in order to obtain a more perfect connection. A platinum anode was used. The gas was collected in an inverted Mohr burette into which the electrolyte was drawn to the stopcock (E). In order that no bubbles of gas might be lost, a funnel was held under the burette by means of a bent glass rod fastened at (B) with a rubber band.

The cathode was introduced into the solution, but no gas was collected until the current had become normal as shown by the voltmeter and ampèremeter. The electrode was then put under the funnel and the duration of the experiment carefully recorded by means of a stop-watch. All variations in the current were also noted by the voltmeter and ampèremeter, and recorded as they occurred. When the burette whose capacity was about fifty to sixty cubic centimeters, was filled, the operation was interrupted and the gas transferred to a Hempel burette. Its volume was then recorded and the gas subjected to analysis. Acetylene was taken out with ammoniacal silver solution in the Bunte-Seger burette, as this is especially adapted for shaking the gas with the absorbent.

In experiment (2) a piece of muslin was tied about the electrode in order to retard the reaction of the dilute acid upon the calcium carbide and thus diminish the amount of acetylene given out. In experiments (4) and (5) a stronger acid, consisting of one part of water and two parts of concentrated acid was used. Experiments (4) and (5) record the results obtained at an anode of calcium carbide. During this operation great deviations in the strength of current were noted. Beginning with 1.2 amp. a sudden fall to .9 amp. occurred. Then came respectively: .8, .7, .9, 1.1 amp., and again a sudden rise was noted to 1.5, 1.6, 1.2, and 1.4 amp.

RESULTS OF THE EXPERIMENTS.

DURATION.	TEMPERATURE.	VOLTAGE.	AMPERAGE.	GAS COLLECTED
I.—90 Sec.	38° C.	50.	2.5–3	25.4 ccm.
II.—20 Min.	31° C.	20.	.5 amp.	40.7 ccm.
III.—10 "	32° C.	51.	.6 amp.	45.2 ccm.
IV.—20 "	25° C.	20.	.2–.3.	18.4 ccm.
V.— 4 "	25° C.	100.	1.6–.7.	43.5 ccm.

GAS SOL. IN WATER.	C_2H_2.	C_2H_4.	H_2.	O_2.	CO_2.	CO.	RESIDUAL GAS.
I.—	5.4	.2	13.7				6.02 ccm.
II.—	4.2	.2					
III.—9.7	2.7	0.					
IV.—				1.8	13.8		12.8 ccm.
V.—	12.1			1.7	2.4	8.5	4.8 ccm.

ELECTROLYSIS OF DILUTE SULPHURIC ACID WITH SLIGHT PRESSURE.

The electrolysis of sulphuric acid accompanied with pressure was performed in a Hoffman's apparatus as shown in figure (4). Only slight pressure was here obtained; namely, that of the weight of the column

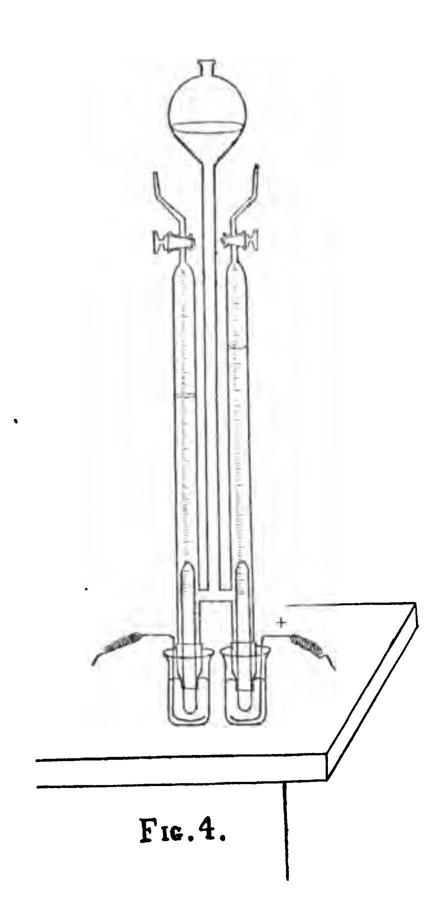


Fig. 4.

of acid about two feet in height. Pencils of calcium carbide were used as electrodes. They were fastened to the lower limbs of the apparatus by a piece of strong soft rubber tubing, and well secured with copper wires in order to prevent leakage of acid. The electrical connections were made by mercury contact. Two small beakers were filled with mercury, and the exposed ends of the calcium carbide electrodes were immersed in the metal beyond the rubber connection. All action of air or of moisture was prevented on the surface of the carbide. In order to wash away the oxide from the calcium carbide it was washed with alcoholic hydrochloric acid, and the alcohol was removed with petroleum. The electrodes were wiped dry with a cloth before the operation. The petroleum oil extracted the alcohol from the electrode and the white crystalline structure of calcium carbide was brought out. When commercial calcium carbide was allowed to remain for some days under petroleum, many impurities were removed and the clear white crystals of the compound could easily be observed. Moissan first showed that chemically pure calcium carbide consisted of these white or transparent crystals.

When the electrodes were thus treated the action of dilute sulphuric acid upon them was diminished. No impurities were introduced into the subsequent products of electrolysis as the oil consisted of saturated hydrocarbons not acted upon during the operation. The acid used in the electrolysis consisted of a mixture of equal parts of strong commercial sulphuric acid (Sp. Gr. 1.82), and distilled water. The current

was allowed to pass for some time before the gas was collected. The anode and cathode gaseous products were separately analyzed.

RESULTS OF THE EXPERIMENT.

	TEMPERATURE.	VOLTAGE.	AMPERAGE.	GAS COLLECTED.
Anode.	18° – 28° C.	115.	.5	72.8
Cathode.	18° – 28° C.	115.	.5	42.4

	ACETYLENE.	ETHYLENE.	CARBON DIOXIDE.
Anode.	12.6		29.7
Cathode.	18.2	0.	

ELECTROLYSIS OF CALCIUM HYDROXIDE SOLUTION WITH CALCIUM CARBIDE ELECTRODES.

As calcium carbide was very quickly and violently acted upon by water, or a dilute solution of calcium hydroxide, some device had to be used to moderate the action. The electrode was soaked for some time in petroleum oil, or when this was not used the electrode was covered with a piece of white muslin. Precipitated calcium hydroxide did not insulate the current as effectively as calcium sulphate. The operation was performed with an apparatus as shown in figure (3). Experiment (2) gave the results obtained at an anode of calcium carbide.

RESULTS OF THE EXPERIMENTS.

DURATION.	TEMPERATURE.	VOLTAGE.	AMPERAGE.	GAS OBTAINED.
I.— 80 Sec.	15° C.	20.	.6	54.8 ccm.
II.—243 Sec.	15° C.	53.	1.2	55.3 ccm.
III. – 63 Sec.	15° C.	53.	1.5	57.3 ccm.
IV.—124 Sec.	85° C.	53.	1.0	46.6 ccm.
V.—105 Sec.	93° C.	20.	.3	39.4 ccm.

GAS SOL. IN WATER.	C_2H_2.	C_2H_4.	H_2.	O_2.	CO_2.	RESIDUAL GAS.
	46.6	.4	3.8			4. ccm.
	42.8			4.	4.	11.4 ccm.
.8	42.5	.6	4.4			9. ccm.
.9	27.4	.8	4.5			13. ccm.
1.5	31.5	2.0	2.3			2.1 ccm.

The precipitate of the electrolysis of calcium hydroxide was analyzed, and a small quantity of carbonate was found to be present; thus accounting for lack of free carbon dioxide in the gas analysis of the anode products. Oxalic acid was also detected as calcium oxalate by the qualitative test. It was likewise determined by titration with a solution of standard potassium permanganate.

ELECTROLYSIS OF CALCIUM CHLORIDE SOLUTION WITH CALCIUM CARBIDE ELECTRODES.

The salts of calcium may be regarded as the typical electrolytes for calcium carbide electrode. In an acid solution the calcium of the carbide becomes a part of the electrolyte as fast as it dissolves, and thus a mixture of electrolytes is avoided. The soluble salts of calcium give up water with great reluctance and even deliquesce in their own water of crystallization. It is easy to regulate the action of the solution of such compounds upon the easily decomposed calcium carbide. In order to obtain good results in the electrolysis of these solutions, concentrated solutions can not be used, as little or no acetylene is given off. It is necessary to add water, or better to dilute the acid in order to insure a sufficient evolution of acetylene. In solutions of calcium chloride and calcium nitrate and

also of zinc nitrate, calcium carbide is practically stable. If ethylene is formed it is not absorbed by the electrolyte. Its presence can be decisively determined without relying on the iodoform test for alcohol when ethylene is calculated volumetrically. If this gas can not be found in the products of electrolysis, it is justifiable to ascribe the iodoform precipitate to aldehyde. If ethylene is not found it is most probable that free alcohol was not present in the products of electrolysis of solutions of sulphuric acid. The object then is to determine whether sufficient ethylene is formed to account for the precipitate of iodoform obtained from the electrolysis of solutions with calcium carbide electrodes.

In the experiments to be described the solutions of calcium chloride was obtained by treating pure calcium carbonate with hydrochloric acid. After filtering the solution it was evaporated to a syrupy consistency. It was not necessary to remove all the acid, as this was afterwards added in order to insure a good action at the surface of the electrode. From this syrupy solution an electrolyte could be obtained that attacks calcium carbide just fast enough to insure a steady stream of acetylene while the electrolysis is in operation. It was found best to add hydrochloric acid rather than to dilute with much water as strong acid solutions attacked calcium carbide more readily than weaker aqueous solutions. The acid served to keep the surface of the carbide electrode free from precipitate of hydroxide or basic insoluble products that acted as an insulator to the current. A solution whose concentration corresponded

to a specific gravity of 1.235, was found to be too strong, for only forty bubbles of gas were obtained per minute. It was further diluted until its specific gravity of 1.2285 at 15.5° C. was denoted, and this electrolyte was found to be best adapted for the process of electrolysis at ordinary temperatures. When the operation was carried at a temperature of 100° C. to 120° C. it was necessary to add more salt in order to obtain a more concentrated solution.

1. — The electrolysis of a solution of calcium carbide was first made with an anode of calcium carbide. A current of one ampère to one and one-fourth ampères was used, and an electromotive force of twenty volts. A quiet evolution of gases took place for some time, but after some minutes explosions occurred under the liquid at the carbide anode. It was not considered safe to collect the gas in quantity owing to the explosive nature of the product. A continuous volley of explosions and a display of sparks took place at the electrode. When an attempt was made to collect the gas in a test-tube the latter was shattered by an explosion. Traces of tetrachloracetylene were obtained in the electrolysis of calcium chloride with a calcium carbide anode.

2. — With the same current the cathode reactions were studied. The apparatus used is shown in figure (5). The cathode consisted of a large piece of calcium carbide. A hole was bored into this and a large copper wire fixed into it with fused lead. The anode consisted of a piece of platinum foil and an ordinary gas cylinder was used as a vessel for electrolysis. To collect the gas a gasometer was at-

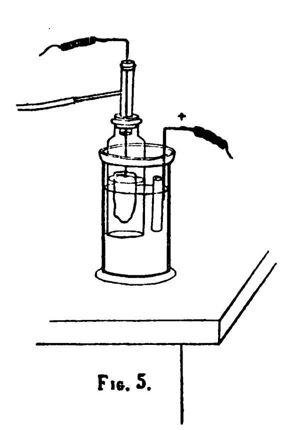


Fig. 5.

tached as shown in figure (2). The entrance of the gas was controlled by allowing water to flow from a siphon which was regulated with a stop-cock (D). The gas was collected at the electrode by means of a wide-necked bottle, whose bottom had been removed. The copper wire (as shown in figure 5) that served as a connection with the electrode was passed through the cork of a Würtz tube and the gas carried off by the side tube. The Würtz tube itself was fitted to the bottle by a large rubber stopper. After continuing the electrolysis for some time the gas was collected and afterwards analyzed. When the experiment was carried on too long the calcium chloride became saturated with acetylene, and explosions took place at the platinum anode. Of 101 ccm. of gas collected, 88 ccm. were acetylene and 1.6 ccm. were absorbed over fuming sulphuric acid, corresponding to ethylene.

3. — The electrolysis of a solution of calcium chloride at a temperature of 100° C. was tried in order to ascertain if different results were obtained from those resulting at ordinary temperatures. The apparatus used was shown in figure (3). Test experiments were first made to find if explosions took place at the anode in the heated solution. After some time it was concluded that the operation could be carried on with safety.

The temperature of the solution in this experiment was 110° C. No explosion occurred with a current strength of .5 ampères and a potential of 10 volts. Again at a temperature of 116° C. and with a current of 1.2 to 1.3 ampères and 20 volts, no explosions were

observed. It was then thought safe to collect some of the gaseous products. In the next attempt a current strength of .5 amp. and 10 volts were used and 42.8 ccm. were collected in three minutes and five seconds. No explosions occurred during the experiment. On examining the gas, 40.2 ccm. were found to be acetylene, thus showing that no free chlorine gas had been obtained. Another operation was performed with a current strength of 1 to 1.1 amp. and 20 volts at a temperature of 112. To prevent accumulation of gas bubbles on the carbide anode, a piece of cloth was tied about it. The gas collected took fire spontaneously in the burette with the separation of carbon. About 31 ccm. of the residual gas were passed into the Hempel burette. All but 18.8 ccm. were absorbed by the water, showing it to be hydrochloric acid gas formed during the explosion. Of the residue 13.8 ccm. were acetylene and neither oxygen or carbon dioxide could be detected.

4.—In the fourth experiment a calcium carbide anode and a platinum cathode were used. With a current strength of 20 volts and 1.1 amp., explosions again resulted at the anode at ordinary temperatures. A black deposit was left on the platinum cathode This was insoluble in dilute or strong hydrochloric acid and somewhat soluble in very strong nitric acid. Heated on platinum no residue was left. It was concluded that the deposit consisted of carbon electrolytically separated. Similar deposits of carbon at the cathode have been obtained by various investigators.

ELECTROLYSIS OF ZINC CHLORIDE SOLUTION WITH CALCIUM CARBIDE ELECTRODES.

Zinc chloride was electrolyzed under similar conditions as already described in the electrolysis of calcium chloride. The salt was prepared from arsenic-free zinc with dilute hydrochloric acid. The apparatus was of the type shown in figure (4). After the solution had been evaporated to concentration, it was used as an electrolyte both at ordinary temperatures and above 100° C. The solution was in one of these operations boiled while the current was passed through it. In the first experiment the anode was a piece of calcium carbide and a zinc rod was used as a cathode. An electromotive force of 20 volts was applied, and this gave a varying current of strength ranging as follows; (.1 amp., .6, 6.5, 4.5, 5, 5.5-6, 6.5, 6.6, 6.8, 7.5, 7.3, 7.6, and finally 8 ampères.)

After the operation the calcium carbide was covered with grains of carbon. No explosion was noticed. A deposit of crystalline zinc took place on the cathode of platinum.

When calcium carbide was used as a cathode in an electrolyte of zinc chloride, no ethylene was obtained. In the third experiment performed with a calcium carbide cathode, and a zinc anode, the carbide became covered with large crystals of zinc The solution of zinc chloride was acidified before the electrolysis, but most of the acid was driven off by the heat of the operation.

In the first experiment no gas was collected. The object of the operation was to find whether chlorine

exploded with nascent acetylene at the anode. It was found that the chlorine united with the calcium of the carbide, while the carbon was separated in a hard gritty mass. Little or no free chlorine was noticed. The temperature of this operation ranged from 124° C. to 132° C. No reason has been found for the great variations of current that were observed.

RESULTS OF THE EXPERIMENTS.

TIME.	TEMP.	VOLTS	AMP.	GAS OBT'D.	C_2H_2.	C_2H_4.	H_2.
	106°C.	20.	5.5	53 ccm	45.2	0.	
II.–3½ min.	100°C.	10.	5.	53.8 ccm	7.3	0.2	23.3

ELECTROLYSIS OF CALCIUM NITRATE SOLUTION WITH CALCIUM CARBIDE ELECTRODES.

Calcium nitrate like calcium chloride is well adapted for electrolytic work with calcium carbide electrodes. In acidified solution the product of reaction of the acid electrolyte upon the electrode is calcium nitrate, and thus mixtures of electrolytes are avoided. Calcium nitrate is as deliquescent as the chloride, and solutions of any concentration may be obtained.

In the first experiment the electrolysis was performed at ordinary temperatures and under atmospheric pressure, in the other operations additional pressure was applied. The apparatus in the first operation was of the type as shown in figure (3), and a cathode of calcium carbide was used. As a concentrated solution of calcium nitrate does not attack the carbide electrode very readily even in the presence of nitric acid, water was added until a good evolution

of acetylene was obtained. The temperature in the first experiment rose from 18° C. to 30° C.

RESULTS OF THE EXPERIMENT.

TEMP.	VOLTS	AMPÈRES.	GAS OBT'D.	C_2H_2.	ABSORPTION BY $H_2S_2O_7$.
18° - 30° C.	10.	2.7 - 3.5.	53.4 ccm	14.4	0.8 ccm.

ELECTROLYSIS OF CALCIUM NITRATE UNDER PRESSURE.

An attempt was next made to electrolyze calcium nitrate solution with calcium carbide electrodes under pressure. In view of the difficulties of obtaining proper connections with the carbide electrode, it was not easy to find a completely desirable method with apparatus that could easily be set from the ordinary laboratory supplies. The apparatus used is shown in figure (6).

The vessel in which the electrolysis was performed was a thick-walled flask having two ground glass openings, and a capacity of 500 cubic centimeters. Into the larger of these openings a calcium carbide electrode (A) was fitted. The smaller opening (B) was closed with a two-holed rubber stopper that was fastened to the apparatus with shellac. Through one of the holes of this stopper passed the tube (C), to conduct the gas into the Hempel burette (D), the amount of gas being regulated by the stop-cock (E). Through the other hole passed the long glass tube (F) which went to the bottom of the vessel and dipped below the surface of a layer of zinc amalgam, (G). This tube was nearly two meters long and was graduated in centimeters throughout. Within

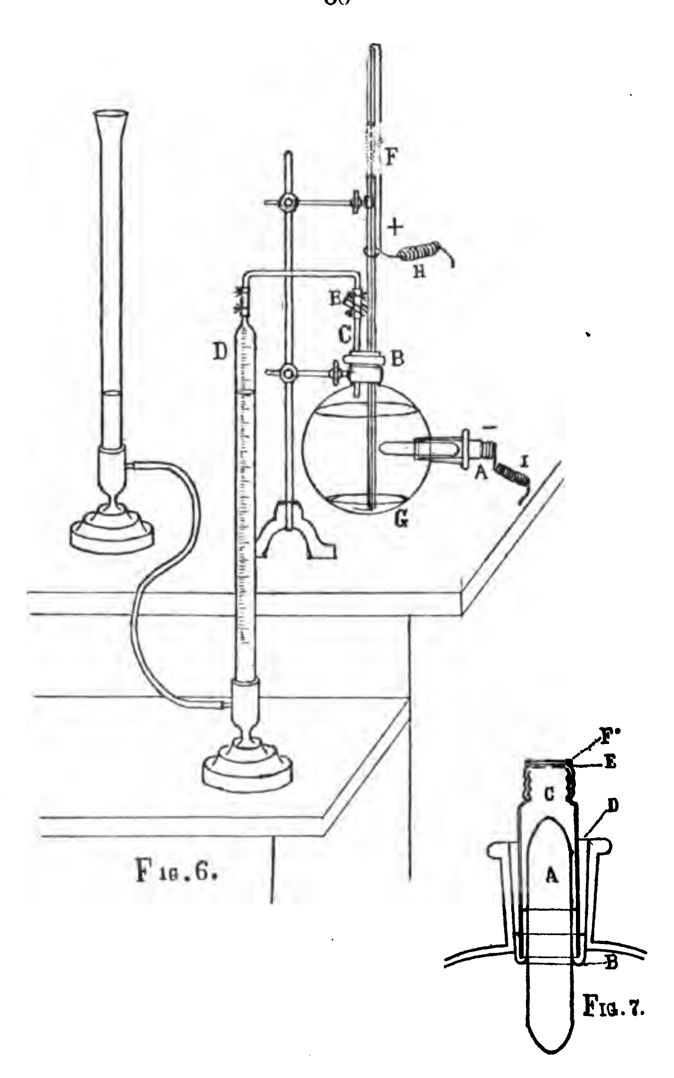


Fig. 6.

Fig. 7.

this passed a small copper wire making connection with the zinc amalgam that served as an anode. The tube served also as a pressure gauge, the amount of pressure being approximately indicated by the height of the mercury in the tube, as the gas increased within the apparatus. The amount of pressure was read off on the tube in centimeters. The function of the amalgam was to reduce the oxygen ions given off at its surface with the formation of water. The acid present in the electrolyte acted on the amalgam giving off hydrogen which united with the oxygen set free to form water.

The gas was allowed to escape only at definite stages and only as fast as it was formed within the apparatus. This was done by regulating the outflow at (G) through the capillary tube and into the Hempel burette. Pure mercury was poured into the long tube to displace the amalgam therein and thus give a correct reading of the pressure.

The calcium carbide cathode is shown more in detail in figure (7) in order to illustrate the connection of the various parts with more exactness. The calcium carbide (A) was made into a pencil of as evenly cylindrical a shape as possible. This was fitted into a small screw-cap specimen-bottle after its bottom has been removed. A piece of soft rubber tubing (B) passed closely and tighty with the carbide into the bottle and was reversed outside of the same. The rubber was well tied to both carbide and bottle, so that any pressure within the apparatus rendered the connections closer, and less liable to leak, and at the same time held the electrode in posi-

tion. Around the bottle was fitted a good cork (D) which was fixed to the opening with asphalt, and allowed to dry several days in an atmosphere free from moisture. The space (C) in the small bottle, not occupied by the electrode was filled with mercury to secure good electrical contact. When good contact was not obtained the heat became so great at the surface of the calcium carbide as to ignite the rubber, owing to the resistance of the cathode to the passage of current. A rubber washer (E) with a hole in its center was inserted above the mercury. The plate (F) of chemically pure iron was put in to prevent the mercury from attacking the metal cap, which was screwed on tightly over the glass bottle.

The circuit was closed after connecting (H) in (Figure 6) with the battery by contact of the wire (I) with the screw-cap of the bottle. The current passed through the iron plate and mercury to the electrode (A), where the gaseous products were evolved.

When the apparatus was ready and the stoppers were well dried, the mercury amalgam was poured into the vessel by a long thistle-tube drawn out at the end. The acidified nitrate solution was poured in through the short glass tube, (C) by inserting within (C) a thistle-tube drawn out to a fine point. The vessel was filled about five-sixths full of the liquid. The apparatus was connected with a Hempel burette and electrolysis begun by making contact at (H) and (I). Two experiments were made and results obtained at three different stages of pressure for each operation.

In the first experiment, the operation was carried on with a current of one-half an ampère and ninety-nine volts electromotive force. When the contact was made the gas was allowed to pass out for some time. Then the stop-cock at (E) was closed, and the mercury rose slowly in the tube (F), as the pressure within increased. When a pressure of 1530 mm. of mercury was obtained, the gas at (E) was allowed to pass into the Hempel burette only so fast, however, as to keep the reading continually at 1530 mm. while the burette was being filled. The stop-cock at (E) was closed and another Hempel burette substituted to obtain products at higher pressure. The experiment was continued with the intention of obtaining the gas at a pressure of 1900 mm. When the column of mercury reached 1860 mm. of mercury in height, the calcium carbide electrode was violently blown out with a loud report.

Another attempt was made after the apparatus had been set up again. The gas was collected at different stages of the experiment:

1.— At ordinary atmospheric pressure.

2.— At a pressure of 1140 mm. of mercury.

3.— At a pressure of 1460 mm. of mercury.

At a pressure of 1610 mm. the cathode was again forced out and thus only three specimens of gas were obtained. Owing to the fact that so little was left after the elimination of acetylene the residues of the three analyses were united and examined for ethylene, hydrogen and ethane. The ethane was determined with the Winckler's pipette and as no diminution of volume occurred, it was then passed into the

explosion pipette over mercury and exploded with a spark from an induction coil. When the gas then passed over caustic potash only 5.4 ccm. of gas were absorbed. Accordingly only traces of saturated hydrocarbons were present.

RESULTS OF THE EXPERIMENTS.

TEMP.	PR'SSURE	VOLT.	AMP.	GAS COLLECTED.	ACETYL'NE
I. — 16° C.	1530 mm.	99.	0.5	58.7	32.4
II. — 16° C.	760 mm.	100.	.1 — .3	82.6	78.6 } to II
III. — 16° C.	1140 mm.	100.	.1 — .3	79.	76.3 } to II
IV. — 16° C.	1460 mm.	100.	.1 — .3	82.	79. } to II

	ETHYLENE.	HYDROGEN.	ETHANE.	RESIDUE OF GAS.
I. —	0			
II. —	2. ccm.	.5 ccm.	2.7 ccm.	4.5 ccm.

ELECTROLYSIS OF NITRATES AT A TEMPERATURE ABOVE 100° C.

ELECTROLYSIS OF CALCIUM NITRATE.

After electrolyzing calcium nitrate at ordinary temperatures, with or without pressure, and not obtaining any marked results as to yield of ethylene at a cathode of calcium carbide, the next attempt was made to electrolyze the same solution at a higher temperature. This experiment was tried with as concentrated a solution as yielded a good quantity of acetylene in the heated electrolyte in the presence of nitric acid. Nitric acid had been added before boiling but most of it was driven off at the boiling point of the solution. Before collecting the gaseous products the current

was allowed to pass for some time in order to obtain a uniform action and a steady flow of gas.

In the first experiment a cathode of calcium carbide was used and a piece of platinum foil as an anode. The apparatus was of the type shown figure (3). Brown fumes of the oxides of nitrogen were given off. After the electrolysis these oxides were reabsorbed by the electrolyte and the operation had to be repeated in order to obtain sufficient gas to submit to analysis. Another constituent of the gaseous product was absorbed in the water of the Hempel burettes after standing for some hours. In the first experiment the gas was passed over caustic potash in order to remove the acid vapors of the oxides of nitrogen.

The first and second experiments record the cathode reactions, whereas the third gives the anode products.

RESULTS OF THE EXPERIMENTS.

TEMPERATURE.	VOLTS	AMP.	GAS COLLECTED.	GAS SOLUBLE IN WATER.
I.— 106.5° C.	10.	5 – 4	40.4 ccm.	1.
II.— 107.5° C.				
-104 5° C.	10.	6 – 5.3	58.5 ccm.	12.5
III.— 110° C.	10.	6 – 4.6	36.8 ccm.	3.

	OXYGEN.	ABSORPTION BY KOH.	C_2H_2.	ABSORPTION BY $H_2SO_4+SO_3$.	HYDROGEN.	RESIDUE.
I.—		10.	8.6	9.	24.	9.
II.—			20.	15.7		
III.—	.4		14.3	10.5		

ELECTROLYSIS OF ZINC NITRATE.

Calcium carbide was used as a cathode in the electrolysis of a concentrated acidified solution of zinc

nitrate. The apparatus represented in figure (3) was used. In all the experiments performed with this electrolyte great variations of current took place. Brown fumes were evolved both at the anode and at the cathode of calcium carbide when a solution was electrolyzed. The operation had to be interrupted several times to allow the acid fumes to be reabsorbed by the solution. In this way sufficient gas was collected to be submitted to analysis.

In the second and third experiment of this series the anode actions were studied. The gas that was collected was allowed to remain in the burettes several days in order to take up acid vapors given off during the electrolysis.

RESULTS OF THE EXPERIMENTS.

DURATION.		TEMPERATURE	VOLT.	AMP.	GAS COLLECTED.
I.—	2½ M.	112.5°–106° C.	10.	3.5–5.	41.
II.—	25Sec.	109° –100° C.	10.	7–5.8.	51.8
III.—		109.5°–116.5° C.	10.	3–5.5	29.8

GAS SOLUBLE IN WATER.		ACETYLENE.	GAS ABSORBED BY $H_2SO_4+(n)SO_3$.	RESIDUE.
I. -		20.6	14.8	
II.—	4.3	39.3		8 3
III.—	17.9	2.4	4 4	

As in the experiments just described in the electrolysis of nitrates at higher temperatures a considerable absorption took place when the gas freed from acetylene was passed over fuming sulphuric acid, it was necessary to ascertain whether it were ethylene. Since, however, the same absorption occurred when the anode products were thus treated it was evident

that the gas could not be ethylene. In order to show that no ethylene was present as a product of the cathode reactions when a heated solution of nitrates was electrolyzed, the experiments were repeated and after all the acetylene had been removed, the residual gas was passed over bromine water in a Hempel pipette and likewise into the Bunte-Seger burette where the gas was shaken with bromine water. Absolutely no absorption was obtained thus clearly showing that the gas was not ethylene nor any other unsaturated hydrocarbon.

The gas could not have been nitrogen trioxide or peroxide as these are absorbed by water or at least by caustic potash. In order to show that the gas absorbed by the sulphuric acid in the pipette was nitric oxide, the gas was collected in considerable quantity. The solution of calcium nitrate was electrolyzed in a flask fitted with a three-holed stopper. The platinum anode was contained in a Gooch tube dipping below the electrolyte so that no gas from the anode could escape into the flask but was carried away as fast as it was formed. A pencil of calcium carbide served as a cathode, and the gas evolved was carried through a tube bent at right angles into a gasometer. The gas was allowed to remain in the gasometer for several weeks to remove all the other oxides of nitrogen. When air was then drawn into the flask the presence of nitric oxide was manifested by the formation of brown fumes of peroxide. The absorption over fuming sulphuric acid was then concluded to be due to nitric oxide according to the reaction :

$$3SO_3 + 2NO = \begin{matrix} SO_2 < \begin{matrix} ONO \\ O \end{matrix} \\ SO_2 < ONO \end{matrix} + SO_2.$$

ELECTROLYSIS OF MERCURIC NITRATE.

In electrolyzing a solution of the salt a cathode of calcium carbide was used in an apparatus as shown in figure (3). As mercuric nitrate is very little soluble in water, a solution was heated with an excess of the solid remaining in the vessel during electrolysis so that the quantity of the solution might remain constant. An anode of platinum was used and nitric acid was added to the solution. Most of the acetylene given off from the electrode united with the mercuric nitrate to form compounds described by Hoffman.[1] The mercuric nitrate did not dissolve fast enough to permit a slow action at the cathode.

RESULTS OF THE EXPERIMENT.

TEMPERATURE.	VOLT.	AMP.	GAS COLLECTED	C_2H_2.	C_2H_4.
87° - 97° C.	50.	.9–1.2.	19.2	8.2	.6

An attempt was made to repeat this experiment, but the solution had become so dilute and the action on the electrode so rapid that of 47.4 ccm. of gas, 32.2 ccm. were found to be acetylene.

In the examination of ammonium nitrate in a heated solution, with a cathode of calcium carbide, a large proportion of acetylene was obtained, ammonia

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[1] Ber. 31, 2213.

gas was evolved, but practically no other gaseous products resulted. Sodium hyposulphite, stannic chloride and various other salts were also electrolyzed with calcium carbide electrodes, but no results were obtained that differed from those already recorded. In the electrolysis of cupric ammonium chloride no gaseous products could be collected owing to the voluminous precipitates that clogged up the burette. The precipitate was first of a light green color, a brown powdery precipitate was then formed and finally it became black. These compounds were, however, formed independently of the action of current, as was subsequently found on heating the double chloride with calcium carbide.

From the results of the investigation just described it is evident that if acetylene unites with nascent hydrogen at the cathode only the faintest traces of ethylene were found. In no experiment performed were more than traces of ethylene at a cathode of calcium carbide obtained. The formation of alcohol at the cathode, mentioned by Bilitzer, does not seem to me to have been sufficiently substantiated.[1] It has been shown that acetylene in the presence of sulphuric acid gave acetaldehyde. This gave the iodoform test as readily as alcohol. Since with unplatinized electrodes no ethylene is obtained at the cathode, it may be concluded that the synthesis of the gas results from catalytic action of the reduced platinum in effecting the union of acetylene and hydrogen. This synthesis was in fact effected by Wilde[1] as

[1] Ber. 7,353. (Bull. d' Acad. Royal. de Belg. 2, XXI., No. 1, 1874.)

already referred to in the introduction to this work. Sufficient ethylene was not formed in Bilitzer's experiment to account for the amount of iodoform precipitate actually obtained from the products of electrolysis of sulphuric acid. As practically no ethylene was obtained the resulting iodoform is to be referred to the formation of acetaldehyde.

In fact, by passing acetylene for some time into reduced platinum suspended in water acidified with dilute nitric acid, aldehyde was formed. When the filtered solution was treated with iodine and caustic potash, an abundant precipitate of iodoform was obtained.

THE CHLORINATION OF ACETYLENE.

HISTORY OF THE REACTION OF CHLORINE WITH ACETYLENE.

The action of acetylene upon chlorine was first observed in 1835 by Edmond Davy,[1] who, in a paper read before the Royal Dublin Society, reported the instantaneous explosion that occurred when the two gases were brought together. No further investigation of this subject seems to have been made until 1860 when Berthelot[2] who had given the hydrocarbon its name, acetylene, declared that the gas mixed with chlorine gave rise to violent explosions in diffused daylight. He thus seems to infer that the sudden decomposition noticed by Davy is primarily due to the influence of actinic light rays. Wöhler[3] two years later refers to the explosiveness of mixtures of chlorine and acetylene, but assigns no cause for the phenomenon.

The same year Berthelot stated the failure to make di-chloride of acetylene, ($C_2H_2Cl_2$), by direct union of the constituents, owing to the violent explosions that resulted.

In 1866, however, Berthelot[4] came to the conclusion

[1] Ann. 23, 144.
[2] C. R., 51, 1044.—Les Carbures D'Hydrogène Paris, 1901.
[3] Ann. 124, 220.
[4] Les Carbures D'Hydrogène t. I, p. 309.

that a mixture of acetylene and chlorine could be preserved in the dark for several days, but that an explosion took place as soon as brought to the light. He found, moreover, that under certain conditions, the exact nature of which he confessed himself unable to determine, the di-chloride of acetylene was formed.

The union would continue quietly for some time, yet finally, and almost invariably a violent detonation, or spontaneous noiseless combustion with the evolution of light and deposition of much carbon resulted. These effects were noticed as well when an excess of chlorine or an excess of acetylene was used, or even when either gas was diluted several times its volume of hydrogen or carbon dioxide. He now refers the cause of the phenomenon to the formation and spontaneous decomposition of the substituted chloride of acetylene, (C_2HCl), which breaks down spontaneously and violently in contact with oxygen of the air. He confesses, however, his inability to assign a definite cause supported by the evidence of experiment. He believes the explosion results because of a "certain molecular inertia" at the moment the gases are mixed, or on calorific phenomena at the point where the reaction begins.

In 1880 some light seemed to be thrown upon the subject by Wallach.[1] He found that when heating dichlor-acrylic acid, or its salts with alkalies or the hydrates of the alkaline earth metals, a gas was given off which took fire spontaneously, or exploded in contact with the air. By diluting the evolved gas with

[1] Ann. 203, 83.

hydrogen and passing it into bromine, he obtained and analyzed the compound, $C_2HCl\ Br_4$ thus showing the composition of the gas to be a substituted chlor-acetylene of the formula C_2HCl. As already stated, Berthelot referred to this substance as the cause of the explosion when acetylene and chlorine are directly united.

In 1884 Schlegel[1] came to the conclusion that the sole cause for the phenomenon of spontaneous decomposition of a mixture of the two gases is the action of light rays. He showed that the mixture could be kept for an indefinite time in the dark, but that the light of a gas flame is sufficient to explode the gases.

Römer[2] two years later assigns another cause for the phenomenon of detonation. He allowed the acetylene he used to stand some time in diffuse daylight, and found that the walls of the glass vessel containing the gas became coated with a brown product. This he supposed to be a polymerized polyacetylene resulting from the di-acetylene (C_4H_2), discovered shortly after by Bayer.[3] Römer referred the explosion of acetylene and chlorine to the impurity just mentioned because of its instability. Acetylene purified by exposure to light before being brought into contact with chlorine, united quietly to form addition products, whereas freshly prepared acetylene always gave rise to a sudden explosion. Römer concludes that acetylene like ethane, ethy-

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[1] Ann. 226, 153.

[2] Ann. 233, 215 and 184, (3) Ann. Chim. Phys. 16,473.—Carb. d'Hyd. vol. 1.

[3] Ber. 18, 2272.

lene, and carbon monoxide are analogous in their action towards chlorine, and like hydrogen, will explode with chlorine only under the influence of the action of rays of light.

In 1872 Berthelot and Jungfleisch effected the chlorination of acetylene by means of antimony pentachloride. This compound absorbs the gas with the formation of a substance corresponding to the formula $C_2H_2SbCl_5$, which separates in well defined crystals. With water, decomposition takes place and on heating, a mixture of di-and tetra-chlorides of acetylene distills over. When the crystalline compound is heated with an excess of antimony pentachloride, pure tetrachlorethane is obtained. In the distillation explosions very frequently occurred. There is also much danger in passing acetylene into heated antimony pentachloride. The reactions of this method of preparing the chlorides of acetylene were represented by the authors by the following equations:

$$C_2H_2 + SbCl_5 = C_2H_2 \cdot SbCl_5.$$

$$C_2H_2SbCl_5 = C_2H_2Cl_2 + SbCl_3.$$

$$C_2H_2 \cdot SbCl_5 + SbCl_5 = C_2H_2Cl_4 + 2SbCl_3$$

Sabanejeff in 1883 repeated these experiments of Berthelot and Jungfleisch[1] in order to obtain the dichloride of acetylene, and the intermediate compound $C_2H_2 \cdot SbCl_5$, but with little success. The absorption of the gas took place with great difficulty, and with very little evolution of heat. Shaking the contents

[1] Ann. 216, 257.

of the flask often gave rise to an explosion. Sabanejeff could not obtain the crystalline compound of acetylene with antimony pentachloride, though he claimed to have continued the process a long time.

Still another cause assigned for the phenomenon of explosion of an acetylene and chlorine mixture is proposed by Nef.[1] He supposes that the decomposition is due to the presence in acetylene of an impurity, as Römer thought. The polyacetylene of the latter author is declared by Nef to be nothing else than an isomeric form of acetylene represented by the formula $C:CH_2$, which he calls acetylidene. The substituted acetylene chloride discovered by Wallach, is according to Nef, to be represented by the formula ClHC:C a derivation of acetylidene, both of these compounds being very unstable and liable to spontaneous and violent decomposion.

In 1898 Mouneyrat[2] threw some light upon the reaction of chlorine and acetylene, and made a thorough study of the nature of the explosion that occurs when the gases are mixed. He obtained acetylene by the action of aluminium chloride upon ethylene chloride. By passing chlorine in the mixture, the acetylene given off reacted forming principally the symmetrical and unsymmetrical tetrachlorethanes. No explosions were obtained in this reaction.

The author proceeds then to show that the phenomenon of explosion in the union of acetylene and chlorine is due to the presence of oxygen. When the

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[1] Ann. 298, 230.

[2] Bull. Soc. Chim. (3d, Ser.) XIX., 445.

two gases, acetylene and chlorine, were allowed to pass simultaneously into a mixture of ethylene dichloride and aluminium chloride, no explosion occurred when proper care was used to exclude air during the operation. The spontaneous quiet combustion of the two gases could not, however, be prevented at the beginning of the action, nor when both gases were passed in too rapidly. An increased yield of acetylene tetrachloride was obtained in this way and this was due to the direct union of the two gases.

The two gases were also united in test tubes over distilled water saturated with salt to drive out oxygen. Union again took place quietly. If oxygen was intentionally put into a test-tube before bringing the acetylene and chlorine together, a violent explosion always occurred. This was supposed to be due to the formation and spontaneous decomposition of the unstable substituted chloracetylene, C_2HCl, discovered by Wallach. Mouneyrat concludes that mixtures of chlorine and acetylene always combine quietly with formation of tetrachloracetylene in diffuse daylight, provided that there be no trace of free oxygen or of compounds susceptible of giving off oxygen.

The author also suggests a method for the preparation of tetrachloracetylene in the laboratory by passing acetylene and chlorine into a mixture of ethylene dichloride and aluminium chloride. An eighty per cent. yield is obtained. At higher temperatures tetrachlorethane in the presence of aluminium chloride is changed to hexachlorethane.

Mixed haloid acetylene compounds containing chlorine have been obtained in various ways analo-

gous to the formation of ethylene derivities of the halogens. Accordingly by treating a solution of iodine trichloride in hydrochloric acid with acetylene. Plimpton[1] obtained monochloriodacetylene. Other chloriodides appear to have been formed which are richer in chlorine or iodine but on raising the temperature of distillation, decomposition sets in with the separation of iodine vapor. The bromochloride of acetylene is prepared from the preceding compound. It cannot be prepared pure from the chloride of bromine. C_2H_2IBr is formed when acetylene is passed into bromine moniodide in water. Other mixed haloids of more complex formulas may have been present in these operations, but could not be separated undecomposed.

In 1883 Sabanejeff[2] published an investigation on the mixed haloid derivatives of acetylene. He succeeded in separating C_2H_2ClBr and $C_2H_2Cl_2Br_2$ by acting upon $C_2H_2Br_2$ with antimony pentachloride. Sabanejeff treated iodine suspended in water with chlorine and then passed acetylene into the solution.

Results like those of Plimpton were obtained. The compounds $C_4H_2Cl_2I_2$ and $C_2H_2Cl_3I$ were thought to be present but could not be separated without decomposition. When C_2H_2ClI was treated with alcoholic potash a gas was given off which the author concluded to be the explosive C_2HCl.

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[1] J. Ch. Soc. XLI., 392.
[2] Ann. 216, 257.

DIRECT ACTION OF CHLORINE GAS ON ACETYLENE GAS.

Although Mouneyrat has quite conclusively shown that the cause of explosion between acetylene and chlorine when brought together is referred to the presence of oxygen, nevertheless very conflicting results have been obtained which either leave the problem more unintelligible, or point to [other accompany causes. Results have been found that point to the fact that simply the presence of oxygen in diffuse daylight is not sufficient explanation for the explosions that occur. Anyone who has studied the results obtained by various investigators, or has tried to attack the problem systematically cannot but be struck by the apparent haphazard with which the explosions take place. In the course of a single experiment it often happens, that now quiet union takes place with the formation of addition products and again, by no apparent change of conditions, the uniting gases form substitution products with violent explosions. If oxygen be the sole cause of explosion, no explanation has yet been offered as to the nature of the action of this element in bringing about the phenomenon. It has been suggested that the substituted acetylene, C_2HCl, is the cause of the violent decomposition of a mixture of acetylene and chlorine. Both Berthelot and Mouneyrat have intimated this, but no attempt has been made to suggest why this compound should be formed because oxygen is present, and why only acetylene tetrachloride is formed under other conditions. The theory holding that the substance, C_2HCl causes explosion when

acetylene and chlorine are united, is based on no other fact than that the compound, C_2HCl itself explodes, and that Wallach prepared this from dichloracrylic acid. No one has, however, shown that acetylene and chlorine mixture gives rise to the chloracetylene refered to, and there is no experimental evidence that validates the supposition.

If the presence of oxygen is sufficient in itself and necessary to cause explosion in a mixture of acetylene and chlorine, then the presence of oxygen ought in every case give rise to violent detonation. I have performed a number of experiments that tend to disprove this assumption. I had undertaken to see whether the temperature of an experiment has any connection with the explosion, but with what result will be seen in the course of this work.

I.—ACETYLENE AND CHLORINE HYDRATE.

Chlorine was passed into water surrounded by a freezing mixture. Frequent shaking was resorted to in order to obtain small crystals of chlorine hydrate. When sufficient hydrate was obtained the product was transferred to a beaker, to insure that no gas collect above the liquid and so render doubtful whether any action that took place be the result of the union of the two gases, or of direct combination with the hydrate. Neither a slow or rapid stream of acetylene caused action with hydrate itself, neither in subdued, diffuse, or direct sunlight. No action was observed between the acetylene and chlorine gases which escaped. All the chlorine was driven out of solution by the acetylene, which was passed

into the hydrate until a temperature of 21° C. was obtained. No trace of tetrachloracetylene was obtained. When bromine was added to the hydrate, the red color disappeared by action of acetylene, but the chlorine remained or was eventually drawn out of solution without any apparent action.

Nascent acetylene did not give different results. Calcium carbide granulated and powdered, showed no chemical action or explosion. When, however, the operation was performed in closed vessels so that both gases mix above the solution, explosion took place accompanied with separation of carbon. The odor of hexachlorethane clung tenaciously to the particles of soot.

2.—ACTION OF A SOLUTION OF ACETYLENE IN ACETONE TOWARDS A SOLUTION OF CHLORINE IN CARBON TETRACHLORIDE AT LOW TEMPERATURES.

Another attempt to unite acetylene and chlorine at lower temperature was made in a different way. Acetone at O° C. dissolves about twenty-five volumes of acetylene. Carbon tetrachloride dissolves twenty-five per cent. of chlorine at the same temperature. Various methods were used to unite the gases in these solutions. Chlorine was passed into a saturated acetone solution of acetylene, and similarly acetylene gas into the chlorine solution of carbon tetrachloride. Spontaneous combustion could not be avoided, especially in closed vessels. Explosions in test-tubes even were very great. No direct action took place within the solution in either case, all the explosions resulted from gas mixtures above the liquid in the vessels.

As the solutions of gases could not be poured into one another directly without spontaneous combustion, one solution was introduced into the other slowly by a dropping funnel dipping below the liquid. The heat of reaction drove out the gases from solution which then burnt with separation of clouds of carbon. In examining the products no tetrachloracetylene was found. The substances formed were chloracetones. The carbon separated was mixed with hexachlorethane in small quantity.

DIRECT UNION OF ACETYLENE AND CHLORINE AT LOW TEMPERATURES.

To test the effect of low temperatures on the action of acetylene and chlorine the gases were, in another type of experiment, passed simultaneously into a long wide tube several inches in diameter. The operation was performed in diffuse daylight on the window-sill outside, at a temperature of .1° to .2° C. The large glass tube was closed below by a two-holed rubber stopper. The chlorine was passed in by a smaller glass tube, and acetylene through another tube bent so as to dip below a layer of water. During one of the experiments the top of the apparatus was left open so that access of air was not excluded. In another experiment the top of the larger glass tube was connected with a large Gooch tube which dipped below water in a beaker. Chlorine gas was first passed into the apparatus and later acetylene. As soon as the latter gas was led in, dense clouds of white fumes appeared, indicating the formation of tetrachloracetylene which in a few minutes began to

condense and trickle down the sides of the tube No explosion took place, no separation of carbon or spontaneous combustion. The gases that escaped did not burn, though both gases were passed in so rapidly that the bubbles in the wash-bottles could not be counted. After the gases had thus been allowed to combine for more than an hour without any sign of explosion or combustion, more than 30 grams of tetrachloracetylene were formed. At the end of one hour, several cubic centimeters of air were introduced with the chlorine into the apparatus. No sign of explosion or combustion was noted, and after another hour had elapsed another expedient was tried to ascertain the effect on the general action. Hitherto the flow of gases, though both very rapid, had been nearly equal with perhaps a slight excess in volume of the chlorine. By quickly and vigorously shaking the acid mixture of bleaching powder the flow of chlorine gas was suddenly very much increased. After a few seconds a faint brown cloud as large as a candle flame began to form at the top of the large tube. This puff of carbon slowly traveled down the tube increasing in size, accelerating in velocity, and becoming darker in color until near the chlorine tube it became a quiet flame. Much carbon was deposited at the lower end of the apparatus. The silent explosion lasted about ten seconds. When the excess of chlorine had been used up, the quiet union of acetylene and chlorine again proceeded with formation of tetrachlorethane.

Another characteristic peculiar to the phenomenon of explosion is, that whenever it occurs it is accom-

panied with the formation of hexachlorethane. The carbon separated by explosion seems to perform some catalytic function in substituting the hydrogen atoms of acetylene with chlorine. During two hours not a trace of hexachlorethane was obtained though over 30 grams of acetylene tetrachloride resulted. During explosion hexachlorethane is principally formed. If the experiment be so regulated that the acetylene is made to burn in an atmosphere of chlorine which is easily done by bringing about a disturbance of the equilibrium in the union of the two gases, such as I have just referred to, the hexachlorethane is formed in sufficient quantity to be sublimed in clear crystals from the carbon mass. It may be likewise separated from the excess of tetrachlorethane by driving the latter over in dry steam. The tarry mass left behind is a mixture of carbon and hexachlorethane — the latter can be separated with ether or by sublimation.

Berthelot in attempting to give an explanation to the explosive nature of acetylene and chlorine mixtures, supposed that the phenomenon was due to the energy of union, so much heat being given off as to cause partial decomposition of the products into hydrochloric acid and carbon.

The formation of hexachlorethane at the moment af spontaneous combustion seems to point to the fact that the explosion of acetylene and chlorine mixtures is due to the energy of reaction between the two gases when brougth together. Acetylene being an endothermic compound gives off great heat in decomposition when substitution compounds are formed, and substitution products are always formed during

explosion of mixtures of the two gases. Even in violent decomposition of very small quantities the peculiar odor of hexachlorethane noticed after explosion can be noted. No other substituted compounds besides hexachlorethane were noticed.

It is also noteworthy that if the experiment is conducted so as to obtain continuous combustion of acetylene and chlorine, little or no tetrachloracetylene is obtained, but the carbonaceous mass is rich in hexachlorethane. This would lead us to believe that the products of substitution are obtained according to a reaction such as the following :

$$2C_2H_2 + 5Cl_2 = C_2Cl_6 + 4HCl + 2C.$$

The heat given off in breaking up a molecule of acetylene and also as a result of forming hydrochloric acid would be sufficient to propagate the explosion in the residue of acetylene and chlorine according to the reaction :

$$C_2H_2 + Cl_2 = 2HCl + 2C.$$

I have noticed, morever, in the preparation of tetrabromethane that if acetylene be allowed to enter too rapidly into bromine cooled by ice water, the same phenomenon of spontaneous combustion or total decomposition with formation of substitution products results owing to the energy of reaction. A very rapid stream of acetylene will cause ignition of bromine vapor. We should then expect that chlorine which is more energetic than bromine in its action would show the same phenomenon of explosion by the violence of the reaction. In fact even ethylene under certain circumstances will explode with chlorine

though not as energetically as in the case of acetylene. Whatever may be the action of oxygen in initiating, or helping the explosion of acetylene with chlorine, it cannot be the sole cause of the phenomenon, or its introduction in the experiment just described would have caused explosion. As a matter of fact not the least effect resulted. Not until after an hour had elapsed did any explosion occur, and then it was induced by other means.

CHLORINE AND ACETYLENE AT THE TEMPERATURE OF BOILING WATER.

Chlorine and acetylene were brought together into a flask of boiling water connected with a condenser. The latter in turn was connected with a closed receiver and several small Wolff flasks containing water and dilute caustic potash. After the water had been boiling some time, chlorine was passed into the apparatus until the air was displaced. Acetylene was then passed into the flask and so regulated as not to exceed one-half the volume of the chlorine entering. An increased flow of acetylene results in an immediate appearance of a flame in the condenser which burns as long as the excess of gas lasts. If the proportion of gases be well regulated no substituted acetylene is formed. As soon as an excess of acetylene occurs, a play of flames is noticed creeping slowly from the lower part of the condenser to the point where the steam condenses. If the whole apparatus be well filled with chlorine previous to the entrance of acetylene no explosion takes place. The flames can moreover, be prevented by regulating the stream of

acetylene gas. It is important to have the flow of acetylene so regulated that union takes place in the flask when diluted with water vapor. The condensed stream carries down with it drops of an oily liquid which was collected, dried, and distilled. It was found to be tetrachloride of acetylene, and had the correct boiling point. A solution of dilute sulphuric acid gave similar results when boiled.

It was noted that when acetylene were diluted in the steam, no explosion in the flask occurred. Any unused excess reaching the condenser was inflamed therein. The play of flames can at will be stopped or started by regulating the flow of acetylene. These facts lead to the supposition that beside the presence of oxygen and the influence of diffuse daylight as a cause of explosion, the energy of reaction between such active agents as acetylene and chlorine, is also a factor not to be overlooked in considering the explosion of the gases.

ACETYLENE AND CHLORINE AT TEMPERATURES ABOVE 100° C.

In order to study the behaviour of acetylene towards chlorine at temperatures above 100° C. the gases were passed into a retort heated in an air-bath to the desired temperature. The gases were dried perfectly. In the first experiment the gases were diluted with hydrochloric acid gas. The acetylene and hydrochloric acid gas were passed through one tube into the heated retort, and chlorine through another tube. The air bath was heated to 230° C. and chlorine was then passed in to displace the air in the apparatus. The retort was as usual, connected

with a condenser, receiver, and wash-bottles to remove any products formed. Under these conditions union of these gases took place quietly, neither explosion or flames were noticed though the operation lasted all day. The interior of the retort was found however, to contain considerable deposit of carbon which was also swept down the jacket of the condenser; thus indicating that quiet combustion had taken place in the dark. About 100 grams of tetrachloracetylene were obtained. It boiled at 147° C. A considerable amount of hexachlorethane was also found. It was removed by separating the tetrachlorethane with steam and extracting the black residue with ether. After evaporating the ether the crystals were sublimed. The yield of oil was not so good as when uniting the gases in the cold. Less oil was obtained in proportion to the amount of acetylene and chlorine used, and the duration of the process.

An experiment similar to the preceding, performed at a temperature of 140° C. gave nearly the same results. The acetylene was not diluted with dry hydrochloric acid acid. The gases were passed into the retort through separate tubes in the proportion of one volume of acetylene to a little more than two volumes of chlorine. The retort in the air-bath was connected with a condenser with closed receiver, and several Wolff flasks containing water and caustic potash. Chlorine was passed into the apparatus first, and then acetylene. After some time carbon was carried over into the inner tube of the condenser which became gradually coated. No explosion of flames were noticed. The flow of chlorine was then suddenly in-

creased in volume, with the result that a play of flame was seen within the condenser, beginning at the bottom and passing slowly to the point of condensation where it continued to burn brightly until the excess of chlorine was used up. This sudden disturbance of the equilibrium of the uniting gases resulted, as in the other experiments, in the formation of substitution products.

As soon as the gases were again regulated carefully the formation of tetrachlorethane continued quietly throughout the greater part of the day until the operation was finished. The products of reaction were, as in the previous experiment, tetrachlorethane and hexachlorethane.

ACTION OF ACETYLENE TOWARDS CHLORIDES AND CHLORINATING AGENTS.

REATION OF SULPHURYL CHDORIDE WITH UNSATURATED ALIPHATIC HYDROCARBONS.

Unlike the other oxy-chlorides, sulphuryl chloride is principally a chlorinating agent. This action of chlorination takes place in many instances by the dissociation of the compound into its derivative components, sulphur dioxide and chlorine, both being present in the nascent state at the moment of reaction. Many substances susceptible of union with the halogens can accordingly take from sulphuryl chloride its chlorine, which are not ordinarily or readily capable of being effected in other ways. In some instances the operation takes place by direct combination, in other cases the addition of aluminium chloride is necessary as an intermediary for the reaction.

Sulphuryl chloride has been used mostly to effect reactions in the aromatic series,[1] and here it manifests its general property of substituting its halogen in the place of one or more hydrogen atoms of those com-

[1] Ber. 15, 1736. Eberhard, Inaug. Dissert. p. 13. (Z 1866, 705.) Eberhard, Diss. p. 11. Ber. 11, 567, J. Pr. II., 17, 322. Wenghofer, Inaug. Dissert. Rostock, 1894.—Ber. 26, 2940. Fram, Inaug. Dissert. Rostock, 1895. Gaz. XXX., 1, 572. Gaz. XXXII., II., 30. Gaz. XXVI., II., 403, (1896.) Gaz. XXIV., I. p. 236, (1894.) Ber. 26, 2940. Gaz. XXVIII., I. 197. Gaz. XXVIII., I., 197, 1898. Gaz. XXIX., I., 340, 371, 383. Gaz. XXIX., I., 554. Gaz. XXXI., I., 464. Gaz. XXXI., II., 184.

pounds. With salts or their acids it behaves like the chlorides of phosphorus, the hydroxyl being replaced with the formation of acid chlorides.

The chlorination of inorganic substances has been shown to be accelerated by the addition to sulphuryl chloride of some aluminium chloride. This increase of activity is ascribed to the power possessed by the aluminium chloride of dissociating the sulphuryl chloride into its component gases, both being present in the nascent condition when a substance is added that is capable of being united either to the chlorine or to the sulphur dioxide. The action of the aluminium chloride in this reaction is somewhat different from its action in the ordinary cases in which it is used as an agent for chlorinatian or condensation of hydrocarbon residues. Ordinarily the action of aluminium chloride seems to be that of forming a compound with a hydrocarbon or an acid chloride. This double compound breaks down an addition of water, and two hydrocarbon or a hydrocarbon and a ketone residues unite together. In case of chlorination, one of the atoms in the chlorine molecule unites with the hydrocarbon residue while the other is joined to the hydrogen atom abstracted from the hydrocarbon to form hydrochloric acid which is evolved in the process of decomposition with water.

Andrianowsky[2] in 1879 discovered that aluminium chloride absorbs sulphur dioxide to form a compound to which he ascribed the formula, $AlCl \cdot {}_2SO_2Cl$. This is syrupy liquid that solidifies at 10° C. to a crystalline mass. On heating it attains the consistency of anhydrous glycerine. On further heating it decom-

poses giving off sulphur dioxide, and disulphur dichloride in small quantity, while aluminium chloride and some aluminium sulphate are left. It is completely decomposed at 140° C.

Now Ruff[1] has shown that when sulphuryl chloride dissolves aluminium chloride the compound, $AlCl_2 \cdot SO_2Cl$, is formed, and on heating the solution, can be obtained at the end of the operation. It is supposed to be present even at ordinary temperatures being formed according to the reversible reaction:

$$AlCl_3 + SO_2Cl_2 \rightleftarrows AlCl_3 \cdot SO_2 + Cl_2.$$

He shows that the compound of aluminium chloride and sulphur dioxide is formed.

It is then concluded that a real catalytic action in the older sense of the word, occurs here; for a single addition of a small quantity of aluminium chloride is sufficient to effect the chlorination of an indefinite amount of sulphur, by starting an accelerated action in the mixture at ordinary temperature.

In the action of aluminium chloride with sulphuryl chloride, the end products are obtained by reason of the formation of the substance $AlCl_3 \cdot SO_2$, or rather because of the affinity between aluminium chloride, $AlCl_3$, and sulphur dioxide when any compound present is capable of forming a stable chloride. The substance $AlCl_3 \cdot SO_2$ is, however, only a bye-product. The chlorination is effected by reason of the tendency of aluminium chloride to dissociate sulphuryl chloride, and unite with the sulphur dioxide given off. This action of

[1] Ber. 35, 4453, (1903.)

[2] Ber. 12, 688, 853.

influence of aluminium chloride in breaking up the sulphuryl chloride molecule has been called by Ruff "dissociation catalysis." The differences discussed can be summed up by saying that in the general aluminium chloride reactions, double compounds are formed which are afterwards decomposed with water. In the other instance, the aluminium chloride instead of uniting with sulphuryl chloride breaks it up to form the compound $AlCl_3 \cdot SO_2$, while nascent chlorine is set free. This action will be well illustrated by the experiments about to be described, namely; the chlorination of acetylene, ethylene, and amylene in the presence of aluminium chloride, by means of sulphuryl chloride.

The chlorination of unsaturated hydrocarbons seems to bring out the nature of the theory of Ruff very strikingly as addition products are formed. The dissociated chlorine unites directly with the hydrocarbon to form saturated compounds. The ordinary chlorination reactions of hydrocarbons of saturated series in the presence of aluminium chloride are operations of substitution and hydrochloric acid is evolved. With unsaturated compounds such as ethylene, and acetylene, hydrochloric acid is not formed but direct union takes place with one or or more whole molecules of chlorine according to the number of uncombined valencies of the hydrocarbon in question.

By far the greatest amount of work with sulphuryl chloride as a chlorinating agent has been done in the aromatic series of the hydrocarbons. A number of interesting reactions have of late been effected with

inorganic compounds. Very few substances in the aliphatic series have as yet been treated with sulphuryl chloride though the side chains of aromatic compounds have been chlorinated in direct sunlight.

Allihn[1] tried the reaction of sulphuryl chloride on acetone and acetoacetic ether, and he obtained mono- and di-substitution products. Roubleff[2] succeeded in chlorinating methylacetoacetic ether to a monosubstitution derivative by using the proper proportions of reagent. Glacial acetic acid[3] gives small quantities of acetyl chloride in the preparation of sulphuryl chloride according to the method of Melsens. The principal bye-product however, is monochloracetic acid. Boiling glacial acetic acid gives more acetyl chloride when treated with sulphuryl chloride. When succinimide is heated in sealed tubes to 100° C. dichlormaleic acid imide is formed which gives rise to dichlormaleic acid when dilute alkalies are added. Behrend[4] obtained from alcohol and sulphuryl chloride according to the conditions of the experiment and the quantities of reagent used, the compounds $\begin{matrix} C_2H_5O \\ Cl \end{matrix} > SO_2$, and $\begin{matrix} C_2H_5O \\ C_2H_5O \end{matrix} > SO_2$. Glycol gave the substance $C_2H_4 < \begin{matrix} OH \\ OSO_2Cl \end{matrix}$. The amines and their chlorides give respectively sulphones or sulphone chlorides of the corresponding substituted ammonia. Piperidine[5] gives rise to sul-

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1 Eberhard, Inaug. Dissert. Rostock. 1894.
2 Ann. 259. 254.
3 Eberhard, Inaug. Dissert. Rostock, 1894.
4 Ber. 17, 9. Ann. 222, 116, 136.
5 Fram. Inaug. Dissert. Rostock, 1895.

phopiperidid. Mercaptan[1] with sulphuryl chloride yields as a final product, after separation of hydrochloric acid and sulphur dioxide, ethyl disulphide

$$\begin{matrix} C_2H_5\cdot S \\ | \\ C_2H_5\cdot S. \end{matrix}$$

Sodium mercaptide was used instead of the alcohol.

The sulphuryl chloride used in the following experiments was obtained from several sources. Some was made according to the method of Melsens,[2] another product was made by the method of Schultz,[3] finally, sulphuryl chloride obtained from Kahlbaum was used. In every case the same results were obtained in the final reactions, yet in some instances the yield of product was smaller owing to the presence of impurities that reacted with aluminium chloride directly, and thus retarted its catalytic action.

CHLORINATION OF ACETYLENE WITH SULPHURYL CHLORIDE IN THE PRESENCE OF ALUMINIUM CHORIDE.

As none of the aliphatic hydrocarbons have as yet been treated with sulphuryl chloride, no conclusion can be drawn whether any difference of action might be found between the behaviour of saturated and unsaturated compounds of the series. The object of the investigations about to be described, is the action of sulphuryl chloride upon the lower members of the unsaturated paraffines, ethylene, and also upon ethylene and amylene.

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[1] Ber. 18, 3178.

[2] C. R. 76, 92, also Eberhard, Inaug. Dissert. p. 8, Rostock, 1894.

[3] J. Pr. Ch. 23, 351. Ber. 14. 989, 2225.

Perfectly dry acetylene does not react with sulphuryl chloride at ordinary temperature. The gas was passed into the chloride for a whole day without the faintest trace of reaction. Even when the contents of the flask were raised to boiling temperature, no better results were perceived. If, however, a small amount of aluminium chloride be added to the sulphuryl chloride, the action is soon made manifest by the heat evolved, or the more or less complete absorption of the acetylene passed in. The contents of the flask were decomposed by being poured slowly into water at low temperature, and a liquid, having the ethereal odor of chloroform was left behind. There were likewise traces of evil-smelling sulphur compounds. These latter reminded one forcibly of a mixture of mercaptan and mustard oil. The residue of organic oil, after standing under water for some twelve hours and being washed with dilute caustic potash solution and then with water, was dried over calcium chloride and distilled. The contents of the distilling flask went over at a temperature ranging from 120° C. to 160° C. then decomposition set in accompanied with the appearance of white fumes and the separation of carbon in a hard gritty mass. Most of the oil boiled between 140° to 145° C. (uncorrected.) Not the least trace of sulphur was found in the latter fraction. Though the material used for distillation was quite small, it was evident that the principal product was tetrachloracetylene, whose boiling point is 147° C.

In accordance with the conclusions arrived at by Ruff, it is evident that the action of aluminium chlo-

ride in the presence of sulphuryl chloride is to accelerate the operation by bringing about chemical dissociation. If, however, chlorine were present in the free state, we should expect according to the results arrived at in the preceding work, that when acetylene were passed into the solution of sulphuryl chloride, explosions would occur. The acetylene, however, was chlorinated to tetrachlorethane without even the phenomenon of spontaneous combustion.

It was noted that in the previous experiment the yield of chloride of acetylene seemed to bear some relation to the amount of aluminium chloride used, since only a small amount of the oil was obtained even after passing acetylene gas into the mixture for many hours. It was supposed that a double compound with aluminium chloride is formed which is decomposed by water, one of the products being tetrachloracetylene. Accordingly, about 150 grams of aluminium chloride were added to 250 grams of sulphuryl chloride, in order to insure complete and rapid decomposition at ordinary temperature. The apparatus used, consisted of a round-bottom flask fitted with a two-holed stopper, one hole for a reflux condenser, the other for a glass tube through which the acetylene was introduced. The acetylene was obtained from an ordinary dip-generator, and was dried by passing through concentrated sulphuric acid in a wash-bottle. To insure complete separation of moisture it was next passed through a drying cylinder containing pieces of calcium carbide of the size of a pea. In this way very rapid streams of acetylene can be effectually dried and the traces of acid carried over from the wash-

bottle of sulphuric acid are also removed by the carbide.

In thus passing acetylene into the mixture of sulphuryl chloride and aluminium chloride the contents, according to the theory of Ruff, ought to be strongly dissociated by the gas, especially when a rapid stream is allowed to enter. No particular care was used to exclude air. In fact air was purposely introduced and no explosion was ever found to take place. Even when heated on a water-bath while the gas was being passed into the mixture, no sign of explosion or combustion was observed. This fact is noteworthy because as Ruff has shown, free chlorine is evolved even at moderate heat.

It was found that it is not necessary to heat the sulphuryl chloride and aluminium chloride to obtain reaction. In fact, much heat is evolved and after passing the gas into the mixture some minutes, the contents of the flask became quite warm. Ordinarily, with small amounts of substance no cooling need be resorted to, but this may be made necessary as decomposition products are formed when the heat is too great. The mixture becomes dark purple or even black. When the flask is moderately warmed by the heat of reaction, the acetylene is absorbed as fast as it can be brought into the apparatus. The contents ought not to be allowed to take on a darker hue than auburn or brown. After some time the heat of reaction slackened and the absorption ceased. The experiment had lasted five hours. The contents of the flask were then poured into several liters of cold water. With constant stirring the decomposition

could be rather quietly effected. A clear amber-colored oil separated at the bottom of the vessel, and at the same time white fumes were given off during the operation. A most penetrating and disagreeable odor was perceived. The fumes also effected the eyes so powerfully as to make it impossible to perform the work except in a well ventilated hood. A painful flow of tears was caused by the least trace of substance decomposed. The following day the irritation to the eyes and the mustard oil smell was less noticeable owing, probably, to the fact that the compound is decomposed on standing some time with water. The clear heavy oil obtained, was washed with dilute caustic potash solution to remove acid traces. It was then shaken with distilled water, dried over fused sodium sulphate, and part dried over fused calcium chloride. The principal fraction of the product boiled at 147° C., and as no trace of sulphur could be found by analysis, it was concluded to be tetrachloracetylene. It possessed an ethereal odor like chloroform mixed, however, with traces of the odor of mustard oil.

When acetylene is passed into the solution or mixture of aluminium chloride and sulphuryl chloride, action takes place almost immediately. Under favorable conditions the dry gas is completely absorbed as fast as it can conveniently be passed into the apparatus. The heat is considerable, and no gaseous products are evolved. If the acetylene leaving the reflux condenser is passed into water, a strong smell of sulphur dioxide is noted. This, however, is due to the decomposition by water of the

sulphuryl chloride carried over mechanically, even through a well cooled condenser. The gas passed into barium chloride, gives rise to an immediate precipitate insoluble in acids, barium sulphate. Moreover, when the action has well started, the reflux condenser may be stopped with a cork, so that no escape for the evolved acetylene is possible. It is still absorbed in a regular stream and without the production of any gaseons product.

When acetylene is made to react with suphuryl chloride in the presence of aluminium chloride, the principal product has been shown to be an addition product acetylene tetrachloride. No other chloride has been separated by fractional distillation, but there is evidently another compound present that possessed the irritating odors just mentioned. Moreover, on heating the acetylene tetrachloride residues, the temperature rose steadily until, at a certain point between 165° C. and 175° C., decomposition set in, accompanied with the separation of carbon and evolution of hydrochloric acid gas. The last fractions also gave evidences of the presence of sulphur. In order to isolate the sulphur compound other methods beside that of fractional distillation had to be resorted to. In the action of sulphuryl chloride on various products, other compounds beside chlorides have been obtained, such as sulphones, sulphone chlorides, even in one instance a disulphide. It was thought probable that beside tetrachlorethane, a sulphone chloride of the formula

$$\begin{array}{l} CH(SO_2Cl)_2, \\ | \\ CHCl_2 \end{array}$$

might exist in the products of reaction. This sub-

substance would bear a relation of acid chloride to acetaldehyde disulphonic acid as ethylidene chloride itself does to acetaldehyde.

In order to purify the tetrachlorethane obtained from sulphuryl chloride, the compound was driven over by distillation in a current of dry steam. The oil thus obtained lost much of its evil odor, while a semi-solid brownish residue was left in the distilling flask. This product could not be purified sufficiently to be analyzed. It is some what soluble in ether, insoluble in ordinary alcohol, but could not be crystallized in a mixture of ether and alcohol. All attempts, to obtain crystals, or any definite compound failed. The tetrachloracetylene thus purified, boiled at 145° C.—148° C., and posessed a nearly pure odor of chloroform. As the temperature rose above 148° C.—150° C., signs of decomposition appeared in the presence of white fumes and separation of carbon. The brownish residue when cooled, deposited crystals more or less clear. Only a very small amount was obtained. They were recrystallized in a few drops of ether when separated from the oily residue. Analysis gave no trace of sulphur; they posessed the characteristic camphor-like odor of hexachlorethane. They were formed from the chlorination of tetrachlorethane in the presence of aluminium chloride.

$$C_2H_2Cl_4 + SO_2Cl_2 + AlCl_3 = C_2Cl_6 + AlCl_3 \cdot SO_2 + 2HCl.$$

Another attempt was made to isolate the sulphur compounds referred to. About seven hundred grams of chemically pure sulphuryl chloride were treated

with acetylene in the presence of aluminium chloride in portions of two hundred to two hundred and fifty grams at a time. Aluminium chloride was added during the operation only as fast as it was dissolved by the sulphuryl chloride. It was found that the action ceased when aluminium chloride had been added in the proportion of one part of this compound to every two, or two and half of sulphuryl chloride by weight.

The products of reaction were united and subjected to distillation on a water-bath under diminished pressure, in order to remove the excess of sulphuryl chloride. About fifty to seventy-five cubic centimeters of distillate were obtained. Before this distillation the small excess of aluminium chloride had had been removed by filtering through glass-wool. A part of the product of reaction of acetylene on the solution of aluminium chloride and sulphuryl chloride solidified to an amorphous mass on standing several months.

Under diminished pressure of 58 to 63 cm., the boiling of the contents of the flask began at 15° C. Together with the excess of sulphuryl chloride an oil came over which was afterward found to boil at 120° C. under atmospheric pressure. It had the odor of chloroform, or ethylene chloride, and posessed no trace of any disagreeable products. The temperature of the distillation was kept near 80° C. under diminished pressure, and when the product ceased to come over, the operation was interrupted.

The residue from the distillation under diminished pressure was then decomposed by pouring it into ice-

water slowly with constant stirring. No violent action took place under these circumstances. An amber-colored oil sank to the bottom of the beaker. It possessed the disagreeable odor already referred to. The oil was distilled in a current of steam, and when the tetrachloracetylene had been driven over, a brown viscous oil was left in the distilling flask. This product became semi-solid on cooling, but it resisted all attempts at purification. It was found to be soluble in ether, and when this was evaporated the mass was left as impure as before. It does not dissolve in alcohol, nor would it crystallize from a mixture of ether and alcohol.

Distillation in a current of dry steam did not, however, remove the evil smelling product completely from the distillate. The oil in the receiver was thoroughly washed with water, and finally dried over fused sodium sulphate. The product was subjected to fractional distillation, and the greater part came over near 147° C. and proved to be tetrachloracetylene. Another fraction boiled quite constantly between 160° C. and 163° C. All the fractions, even those with the lowest boiling points, possessed the smell of mustard oil, and sulphur was found in analysis. When decomposition began at 170° C. the operation was stopped. The residue possessed the unbearable odor of allyl mustard oil.

The oils were at last separately washed with a dilute solution of caustic potash. The solution took on yellowish tint and considerable heat was evolved. Each fraction diminished very much in volume. All the fractions were then separately redistilled and

found to have the same boiling point as before. The wash water was evaporated down on a water-bath, and after potassium chloride had come out, an impure salt of a sulphonic acid crystallized out. It was not acetaldehyde disulphonic acid as its oxime could not be prepared. The salt is but slightly soluble in ether which removes all impurities. A very small amount was thus obtained pure by recrystallization from alcohol. Not enough was obtained, however, for analysis.

The oils after repeated fractional distillation remained constant only at the boiling point of tetrachlorethane. They seemed to be purer than before, but the fractions that came over at higher temperatures still possessed the odor of mustard oil. Tetrachloracetylene could with certitude be shown to be present. The fraction coming over under diminished pressure, as also part of the decomposed oil, both of which products boil very constantly at 120° C. were very probably tetrachlorethylene obtained by decomposition of tetrachloracetylene in the presence of aluminium chloride and sulphuryl chloride with application of heat.

$$C_2H_2Cl_4+SO_2Cl+AlCl_3=C_2Cl_4+2HCl+AlCl_3{\cdot}SO_2.$$

At 160° — 163° C., a considerable fraction was obtained with a remarkably constant boiling point.

According to the theory of dissociation catalysis advocated by Ruff, it is supposed that sulphuryl chloride is dissociated in the presence of aluminium chloride as represented by the equation.

$$AlCl_3+SO_2Cl_2 \rightleftharpoons AlCl_3{\cdot}SO_2+Cl_2.$$

A solution of aluminium chloride in sulphuryl chloride was put into a flask connected with a well cooled reflux condenser. The latter was in turn connected with a long tube bent at right angles and entering another flask into which acetylene was passed. The last flask was connected with a condenser and receiver. Twenty-five grams of sulphuryl chloride and twenty grams of aluminium chloride were thus treated to demonstrate the presence of free chlorine. If this gas be given off, it would be shown either by its union, or explosion with acetylene in the second flask. It was found that considerable heat was required before the presence of free chlorine could be detected by its color and odor. A few drops of tetrachloracetylene were obtained from the union of the two gases. By heating the aluminium chloride mixture in the first flask chlorine was freely evolved and met the acetylene in the second flask. Vapors of chloride were effectually kept back by the condenser. No explosion was obtained and no precautions were made to avoid one. Acetylene was allowed to enter the apparatus before the chlorine was evolved, contrary to the usual method of bringing the gases together. In the case of acetylene, the first part of the supposed reversible reaction was found to hold good, and the presence of tetrachlorethane is due to the union of acetylene with the dissociated chlorine of the compound, while the sulphur dioxide unites with the aluminium chloride.

$$SO_2Cl_2 + AlCl_3 = AlCl_3 \cdot SO_2 + Cl_2,$$

$$2Cl_2 + C_2H_2 = C_2H_2Cl_4.$$

In order to satisfy myself as to the assumed reversibility of the reaction of the dissociation of sulphuryl chloride, I have tried to effect the same experimentally. It appears that in order to demonstrate the fact, the attempt should have been made to unite chlorine with the compound, $AlCl_3 \cdot SO_2$ to form sulphuryl chloride.

$$AlCl_3 \cdot SO_2 + Cl_2 = AlCl_3 + SO_2Cl_2.$$

Unless under certain conditions this can be actually effected, it cannot be assumed that, the equation is reversible. It was found impossible to effect a reaction between chlorine and the compound, $AlCl_3 \cdot SO_2$, though it was tried in several ways and under varied conditions. Neither at ordinary temperature nor with the aid of heat have I been able to obtain any sulphuryl chloride. Until sulphuryl chloride shall have been made from the substance, $AlCl_3 \cdot SO_2$, and and free chlorine, it does not seem justifiable to postulate the reversible action.

$$AlCl_3 + SO_2Cl_2 = AlCl_3 \cdot SO_2 + Cl_2, \text{ or,}$$

$$Cl_2 + AlCl_3 \cdot SO_2 = AlCl_3 + SO_2Cl_2.$$

Moreover, the theory of Ruff seems just as valid without assuming that the action is reversible. Reversibility is unnecessary to explain the facts. It is sufficient that aluminium chloride dissociates sulphuryl chloride in the presence of a third substance capable of forming a more stable chloride. Under these conditions chlorination will take place often without raising the temperature by external heating.

In chlorinating acetylene with sulphuryl chloride in the presence of aluminium chloride, no explosion or spontaneous combustion was ever noted, though no precautions were used in excluding air or direct sunlight. It has been shown that chlorine is present even at ordinary temperatures in the mixture of aluminium chloride and sulphuryl chloride. I have passed a mixture of dry air and acetylene into sulphuryl chloride without noticing explosion or combustion. On the contrary, quiet union of acetylene and chlorine resulted, with the formation of tetrachloride of acetylene. This seems very strange if, according to Mouneyrat, the principal cause of explosion of acetylene with free chlorine is to be referred to the presence of oxygen. In view then of this fact, we should be led to conclude that either free chlorine is not present at ordinary temperatures in the aluminium and sulphuryl chloride mixtures, or prior to and independently of the presence of oxygen another cause must operate to initiate the explosion of free chlorine and acetylene when brought together.

The phenomenon of explosion or spontaneous combustion was not found to occur even when the mixture of aluminum chloride and sulphuryl chloride was heated while acetylene was being passed into the flask. The operation was performed on a water-bath so that the contents boiled vigorously. The reflux condenser remained open to the air, and no precautions were made to exclude air. Owing to the heat, signs of decomposition set in as soon as the acetylene was passed into the mixture. The yield of tetrachloracetylene was poor as tarry products

were formed. This was probably due the direct union of sulphuryl chloride with acetylene under these circumstances to form sulphonechlorides of acetylene.

CHLORINATION OF ETHYLENE WITH SULPHURYL CHLORIDE IN THE PRESENCE OF ALUMINIUM CHLORIDE.

Ethylene, like acetylene, does not act on sulphuryl chloride alone, at ordinary temperatures. No traces either of chlorides or sulphonechlorides could be thus obtained. If, however, some aluminium chloride be added, absorption slowly takes place. The action can be accelerated by frequent shaking of the mixture.

The union was effected in a Bulterow's apparatus. The ethylene was made in the usual way, from sulphuric acid and alcohol. The gas was purified by passing it through strong sulphuric acid and caustic potash solution, and was collected in a gasometer. It was dried by passing it through strong sulphuric acid and a drying cylinder containing fused calcium chloride, and then absorbed in the Bütlerow's apparatus containing a solution of aluminium chloride in sulphuryl chloride. Very little rise in temperature was noticed. After the absorption ceased, the contents were decomposed by pouring them into cold water. An oil was left that had an ethereal odor like chloroform mingled with traces of the odor of mustard oil. The product was washed with a dilute solution of caustic potash, then with water, and was finally dried over fused calcium chloride. One half of the product distilled on a water-bath, and was afterward found to boil exactly at 83° C. It was very pure and did not

possess the odor of mustard oil. The second fraction had the odor of chloroform, and consisted of a mixture of higher boiling chlorides and sulphonechlorides with a very disagreeable odor. Attempts to distill it soon ended by decomposition and charring of the contents of the flask. Acetylene tetrachloride was probably the principal product of the second fraction, as Mouneyrat has shown that ethylene chloride is further chlorinated in the presence of aluminium chloride and free chlorine especially when external heat is applied. In the case in question the chlorine came from sulphuryl chloride present, which further reacted with ethylene chloride according to the reaction.

$$C_2H_4+2SO_2Cl_2+2AlCl_3=C_2H_2Cl_4+2HCl+2AlCl_3 \cdot SO_2.$$

In order, if possible, to separate the substance which possessed the odor of mustard oil, and which was most likely a sulphonechloride of ethylene, about 250 grams of sulphuryl chloride were treated in the presence of aluminium chloride with ethylene gas. Aluminium chloride was added in small quantities from time to time only as fast as it was used up in the reaction. Ethylene is not readily absorbed by the mixture, and so it was thought best to aid the action by heating gently on a water-bath. The operation was carried on in a round bottom flask fitted with a reflux condenser. When the gas has been passed through the mixture for some time, the contents of the flask took on a dark color. Towards the close of the action aluminium chloride ceased to be dissolved.

The product was then distilled on a water-bath, and a clear oil came over between 35° and 45° C., under a pressure of 500 mm. This was mostly pure ethylene chloride mixed with an excess of sulphuryl chloride. The latter was decomposed with water and the residue when washed, dried, and distilled, was found to boil at exactly 83° C. under atmospheric pressure. The whole liquid came over to the last drop at the boiling point of ethylene chloride. The product remained pure and retained its characteristic pleasant odor for many months, thus showing it to be umixed with any impurities whatever. Unlike ethylene chloride made by direct union of the gases it did not become pink colored on standing, neither was a disagreeable odor noticed even after half a year. The method seems well adapted for the rapid preparation of pure ethylene chloride in the laboratory.

The residue was cooled with ice-water and then decomposed with very cold water. The disagreeable odor was noted as before. A dirty, pasty mass was left, which seemed to indicate the presence of a large quantity of tarry products. It was subjected to distillation on a water-bath, and impure ethylene chloride was obtained. The residue was then heated on a Babo air bath, and signs of decomposition were noticed before the temperature of 150° C. was obtained. Hydrochloric acid fumes were given off and carbon separated. After this initial decomposition had ceased, a heavy oil distilled at 200° C. Dense white fumes were evolved from it in presence of moist air. It possessed the odor of mustard oil, and the other characteristics of isethionyl chloride which boils

at 200° C. It was very very impure, however, and contained empyreumatic products. Chlorsulphone chloride of ethylene was formed according to the reaction.

$$C_2H_4 + SO_2Cl_2 = \begin{matrix} CH_2SO_2Cl \\ | \\ CH_2Cl \end{matrix}$$

AMYLENE AND SULPHURYL CHLORIDE.

Though acetylene and ethlene did not react with sulphuryl chloride unless the action be accelerated by means of aluminium chloride, amylene on the contrary reacted directly. When even small quantities of the compounds were brought together, amylene broke up the sulphuryl chloride molecule with almost explosive violence. A few drops of each in a test-tube gave off much heat in union and in a few seconds boiled so strongly as to dash the contents out of the tube. Chlorides of pentane were formed.

Accordingly, it was found necessary in chlorinating the compound with sulphuryl chloride, to dilute the amylene by dissolving it in twice its weight of chloroform, and cooling the flask with a freezing mixture. A reflux condenser was attached to the flask containing 50 grams of amylene dissolved in 100 grams of chloroform. About 100 grams of sulphuryl chloride were slowly allowed to enter the flask from a dropping funnel. An immediate action took place. When the union was effected rapidly, the contents gave off so much heat as to boil in a freezing mixture, sulphur dioxide being evolved. Nearly an hour was needed to introduce all the sulphuryl chloride. After the action was completed, the flask was moderately warmed and sulphur dioxide driven out. The con-

tents are distilled on a water-bath, when the excess of chloroform was separated, mixed with a small quantity of sulphuryl chloride. Sulphur dioxide gas remained in solution. The chlorides of amylene were then fractionated. Below the temperature of 130° C. a mixture of chloroform and some amylene chloride distilled. Amylene chloride itself came over from 130° C. to 140° C. Trichlorpentane was also formed and went over at higher temperatures together with amylene chloride. The higher boiling fractions possessed the characteristic camphor odor and taste of trichlorpentane. The reactions may be represented as follows:

$$C_5H_{10}+SO_2Cl_2=C_5H_{10}Cl_2+SO_2.$$

$$C_5H_{10}Cl_2+SO_2Cl_2=C_5H_9Cl_3+HCl+SO_2.$$

The amylene which was used boiled at 45° C. Both the hydrocarbon and the chloroform were previously dried perfectly with fused calcium chloride. When aluminium chloride was added tarry products were formed, and solids resulted having a rather unpleasant camphor odor, but the yield of amylene chloride itself was not good. No sulphur compounds were noticed when aluminium chloride was not used. The higher fractions underwent partial decomposition in rectifying, carbon was separated and hydrochloric acid was evolved.

BEHAVIOUR OF ACETYLENE TOWARDS OTHER CHLORIDES AND CHLORINATING AGENTS.

ACETYLENE AND DISULPHUR DICHLORIDE.

When acetylene was passed into disulphur dichloride kept boiling in a flask with a reflux con-

denser, the gas was very slowly absorbed. The action, however, was very imperfect. When the product was decomposed with water an organic oil is left in small quantity. It was very impure, mixed with sulphur and possessed a disagreeable alliaceous odor. The precipitate of free sulphur retained this odor for a long time after decomposition with water. When aluminium chloride was added to the disulphur dichloride into which acetylene had been passed for several days, an immediate and strong reaction took place accompanied by a change of color of the contents of the flask from clear yellowish red to opaque brown. When acetylene was passed into disulphur dichloride in the presence of aluminium chloride, the gas was completely absorbed with the evolution of so much heat that the flask had to be cooled with water, or the flow of gas temporarily diminished to prevent total decomposition of the products formed. Towards the end of the reaction the mixture of disulphur dichloride and aluminium chloride tended to solidify on exposure to the air. Fractional distillation, even under diminished pressure, failed to separate the compounds formed. Decomposition took place before a temperature of 140° C. was reached. The first fraction of the distillate was of a light straw color, and possessed the characteristics of thiocarbonyl chloride. It fumed strongly in the air. At a temperature of 74° C. and 300 mm. pressure it began to distill. The color of the distillate became a darker red between 121° C. and 141° C. under 350 mm. pressure. At 160° C. a beautiful violet colored product distilled, and almost simultaneously decomposition set in with

the separation of carbon, sulphur, and hydrochloric acid. The carbon separated in hard compact form like coke. One of the products of decomposition was a greasy black product which separated with the violet oil above 160° C. The oil could not be redistilled under atmospheric pressure without undergoing decomposition. On decomposing the product of reaction a very small quantity of impure acetylene tetrachloride was obtained. When the product of the reaction of acetylene with disulphur dichloride in presence of aluminium chloride was decomposed before distillation by pouring it into well cooled water, acetylene tetrachloride in very impure condition mixed with alumina and sulphur, was obtained.

Guthrie[1] has shown that ethylene forms additional compounds with disulphur dichloride, when the gas was passed into the heated compound. Substances of the formula, $C_2H_4Cl_2 \cdot S_2Cl_2$, and $(C_2H_4)_2 \cdot S_2Cl_2$, were obtained.

Attempts were made to obtain the similar acetylene compounds that might be formed by the action of dry acetylene upon aluminium chloride and disulphur and dichloride. The products of the reaction were decomposed with water, and a solid mass containing sulphur and tetrachlorethane was extracted with several liters of ether, in which the compound is somewhat soluble. After evaporating the ether, an oily residue was left that crystallized in radiating needles, slightly tinged with a purple violet. It was mixed

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[1] Jour. Chem. Soc. XIII., 35, 129, XIV., 128. Ann. 113, 266, and 116, 234.

with tetrachlorethane and disulphur dichloride. The crystals could not be purified or separated from the other products. The extract with carbon disulphide instead of ether, underwent general decomposition, carbon, sulphur and hydrochloric acid being the final products.

ACETYLENE AND SULPHUR DICHLORIDE, (SCl_2).

Acetylene was absorbed more readily by sulphur dichloride than by disulphur dichloride, but as the former gave off free chlorine, it was necessary to cool the flask with ice-water and carefully to regulate the stream of acetylene, in order to prevent spontaneous combustion of the escaping gases. By allowing the acetylene to enter the compound through a capillary tube all danger of explosion was obviated. The escaping gases were at times spontaneously inflamed at the beginning of the operation. This occurred especially when they were allowed to bubble through water, the gas bubbles then exploding on contact with the air. There was reason to believe that a great part of the acetylene absorbed was not chemically acted upon but only held in solution. When aluminium chloride was added to the contents of the flask after passing in acetylene some hours, a sudden and violent reaction takes place, accompanied with combustion of the evolved gases, and separation of carbon. The residue took on a dark brown color and became very hot. Hydrochloric acid was slowly evolved. The products of the reaction after adding aluminium chloride and continuing the absorption of acetylene were apparently the same as in the case of disulphur dichloride. Frac-

tional distillation even under diminished pressure did not give pure products. More tetrachloracetylene was obtained than in the previous experiment. The study of the action of acetylene upon the chlorides of sulphur will be continued.

ACETYLENE AND VARIOUS OTHER CHLORIDES.

(THIONYL CHLORIDE, $SOCl_2$).

Acetylene did not react with thionyl chloride even in the presence of aluminium chloride at oridinary temperature. When the mixture of chlorides was heated while acetylene was passed into the compounds, tarry products were obtained possessing a very disagreeable odor like that of the sulphone chlorides of the aromatic series. Small quantities of the products of reaction were obtained as a dark brown gummy mass, on decomposing the contents of the flask with water.

(STANNIC CHLORIDE, $SnCl_4$)

Pure anhydrous redistilled stannic chloride, free from chlorine, did not give up part of its chlorine to acetylene even in the presence of aluminium chloride. When the heat was applied, acetylene was decomposed in part, leaving hard particles of carbon floating in the liquid, but no chloracetylene was obtained. The stannic chloride boiled at 114° C. and was pure and perfectly anhydrous.

PLUMBIC CHLORIDE, ($PbCl_4$), AND PLUMBIC AMMONIUM CHLORIDE, ($PbCl_4,2NH_4Cl$).

When acetylene was passed into the solution of plumbic chloride in strong hydrochloric acid, explosions took place by reason of the free chlorine

constantly evolved from the compound. Crystalline plumbic ammonium chloride has been found to give up chlorine readily to aromatic hydrocarbons. Acetylene, however, gave no chlorine reaction products even in presence of aluminium chloride, nor when both chlorides were dissolved in another liquid chloride, such as phosphorus trichloride. When calcium carbide is heated with plumbic ammonium chloride, a violent reaction takes place, but no acetylene chloride was obtained. The products seemed to be similar to those made by Salvadori[1] by the action of ammonium chloride on calcium carbide. As no acetylene chloride was obtained, the action of acetylene with plumbic chloride was not further investigated.

CARBONYL CHLORIDE ($COCl_2$), CYANOGEN CHLORIDE ($CNCl$), NITROSYL CHLORIDE ($NOCl$).

None of these gases showed any reaction whatever with acetylene. Carbonyl chloride and nitrosyl chloride were also passed with acetylene over aluminium chloride without any signs of union. The latter in the nascent condition evolved from nitrosulphonic acid, sodium chloride, and sulphuric acid failed to give any organic compound when acetylene was passed into the mixture.

ANTIMONY TRICHLORIDE, ($SbCl_3$), AND PHOSPHORUS PENTACHLORIDE, (PCl_5),

When antimony trichloride and aluminium chloride were heated together while acetylene was passed over the compounds, only traces of tarry products were

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[1] Gaz. XXXII., II., 496, (1902).

obtained possessing very disagreeable odors. Phosphorus pentachloride did not give up part of its chlorine to acetylene even in the presence of aluminium chloride. When a solution of phosphorus pentachloride and aluminium chloride in phosphorus trichloride was heated below the dissociating point of phosphorus pentachloride while acetylene was passed into the boiling mixture, no better results were obtained. Only traces of ill-smelling organic compounds were found on decomposing the product of reaction. When phosphorus pentachloride was further heated, it dissociated. Explosions took place whenever acetylene was passed over it at higher temperatures.

CHROMYL CHLORIDE, (CrO_2Cl_2).

As this compound gives off free chlorine very readily, and is likewise a powerful oxydizing agent, violent explosions would be expected when acetylene is passed into chromyl chloride. In fact, every attempt to introduce acetylene into the flask containing this substance ended in an explosion or spontaneous combustion of the gas and separation of carbon.

ARSENIC TRICHLORIDE, ($AsCl_3$).

Pure arsenic trichloride free from oxide did not show any reaction with perfectly dry acetylene. When aluminium chloride was added the absorption of the gas was effected with the evolution of considerable heat. The contents of the flask turned black. When decomposed by pouring the substance into cold water, a black gummy mass separated out, and on standing for some time crystals appeared in the aqueous solution. The tarry substance possessed a most

nauseating and penetrating odor, and was extremely poisonous. Inhalation of the fumes, even in small quantity caused nervous depression. No chlorine derivatives of acetylene were noted. Owing to the poisonous nature of the compounds formed, their thorough investigation was postponed.

ACETYLENE AND DRY IODINE TRICHLORIDE, (ICl_3).

The action of acetylene upon iodine trichloride in solution of strong hydrochloric acid was studied by Plimpton and Sabanejef. Monochlormoniodacetylene was formed. Chloriodacetylenes were formed with more than one atom of chlorine in the molecule and could not be distilled, as they decomposed with the separation of iodine at 120° C.

To obtain the crystals of iodine trichloride, iodine was heated in a retort while a stream of dry chlorine was passed into the vapor. Connected with the retort was a flask with two ground glass openings. The neck of the retort was fitted into one of these so that it was not necessary to use rubber or cork connections. The trichloride was sublimed into the flask in a stream of dry chlorine, care being taken that no iodine monochloride was allowed to pass over. When all the trichloride was sublimed into the receiver chlorine was passed for some time to get rid of the traces of monochloride of iodine. The well-stopped receiver containing the iodine trichloride in an atmosphere of chlorine was then put aside for twenty-four hours.

Acetylene was then passed in through one of the openings by means of a capillary tube. The gas was absorbed as fast as it entered, and more acetylene was

drawn in by reason of the vacuum created by absorption, as the other opening of the flask was kept closed with a cork. The heat evolved in the reaction was considerable, and the flask was cooled by a stream of cold water. The first stage of reaction seemed to be that of chlorination, as iodine monochloride was separated as soon as the acetylene entered. No explosion occurred. As soon as all the iodine trichloride had disappeared, the operation was immediately interrupted, and the free iodine and iodine monochloride removed from the oil which was then clear and odorless. The dried product was distilled. Very little distillate was obtained below 126° C. The temperature then rose to 146° C., when much iodine separated and the greater part of the oil distilled over. Monochlormoniodacetylene boiled between 116° and 119° C. And therefore, little if any was present. Acetylene tetrachloride was the principal or at least the first product of reaction between acetylene and dry iodine trichloride. Chloriodacetylene was the result of a secondary reaction. The fact that iodine monochloride comes out as soon as acetylene reacted with the solid trichloride of iodine, sufficiently demonstrated this. The trichloride of iodine then, acted as a chlorinating agent, and when the operation was interrupted after all the trichloride of iodine was used up, very little if any acetylene iodochloride, C_2H_2ClI, was obtained. The reaction may be represented as follows:

$$C_2H_2+2ICl_3=C_2H_2Cl_4+2ICl.$$

When an excess of acetylene is present, the iodine

monochloride reacted further with the hydrocarbon to form monochlormoniodacteylene according to the reaction :

$$C_2H_2+ICl=C_2H_2ICl.$$

Other reactions forming compounds of acetylene with chlorine and iodine containing more than one atom of chlorine took place independently of those referred to. It is also noteworthy that a compound as easily dissociated as iodine trichloride in the dry state does not explode with acetylene.

ACETYLENE AND "AQUA REGIA."

The chlorinating action of "aqua regia" is said to be due to the evolution of chlorine in the nascent state when the mixture is warmed, and this effect is produced according to the reaction:

$$3HCl+HNO_3=2H_2O+NOCl+Cl_2.$$

When acetylene was passed into "aqua regia" at ordinary temperature or even at the boiling point of the solution, no explosion or spontaneous combustion was ever observed, though air was present during the operation. The gas was passed into the acids both in a slow and rapid stream. Evident signs of reaction were noted by the formation of an oil in small quantity. Even the small quantity that was formed seemed to be decomposed by the continued action of the "aqua regia." The presence of hexachlorethane was observed. Small acicular crystals of this compound floated in the acids, but the yield of tetrachlorethane and hexachlorethane was very small. The latter compound resulted from the con-

tinued action of nascent chlorine on the tetrachloride of acetylene when the latter was not immediately removed from the scene of action by distillation. The reaction may be expressed as follows:

$$3HCl + HNO_3 = H_2O + NOCl + Cl_2,$$

$$2Cl_2 + C_2H_2 = C_2H_2Cl_4,$$

$$C_2H_2Cl_4 + 2Cl_2 = C_2Cl_6 + 2HCl.$$

When dry hydrochloric acid gas were passed into fuming nitric acid, no chlorine derivatives of acetylene were obtained. Nitro-compounds of acetylene were obtained when the acid was diluted with water.[1]

When very strong hydrochloric acid (Sp. gr. 1.20) was boiled with strong nitric acid while a rapid stream of acetylene was passed into the flask connected with a Liebig condenser, tetrachloracetylene was obtained in greater quantity. It contained, however, as an impurity a nitrogen compound with a penetrating odor which caused a painful flow of tears. Its solution in the oil gave to the latter a pale green color.

So strong a reagent as "aqua regia" did not cause any explosion with acetylene though free chlorine was present. Moreover, air was present in all these experiments and not the slightest trace of carbon was separated. When nascent acetylene was used, reactions with "aqua regia" gave the same results, tetrachlorethane and hexachlorethane being obtained. This was accomplished by throwing pieces of calcium carbide into the acid. Calcium carbide decomposed

[1] Gaz. XXXII., I., 202, (1902). Gaz. XXXI., II., 465, (1901).

rather slowly in the mixture, and hexachlorethane was the principal product. In this case no spontaneous combustion or explosion resulted, though very much heat was evolved from the decomposition of the calcium carbide.

ACETYLENE AND ANTIMONY PENTACHLORIDE, ($SbCl_5$).

The method of preparing tetrachlorethane by means of antimony pentachloride and acetylene, discovered by Berthelot and Jungfleisch[1] in 1872, might be considered a more or less convenient way of preparing that compound. When acetylene was passed into antimony pentachloride, the gas was more or less readily absorbed, varying with certain conditions not as yet well determined. On cooling the contents of the flask crystals of the compound, $SbCl_3 \cdot C_2H_2Cl_2$, separated out. When these were heated, a mixture of tetrachloracetylene was supposed to be formed according to the reactions:

$$C_2H_2 + SbCl_5 = SbCl_3 \cdot C_2H_2Cl_2,$$

$$SbCl_3 \cdot C_2H_2Cl_2 = C_2H_2Cl_2 + SbCl_3,$$

$$SbCl_3 \cdot C_2H_2Cl_2 + SbCl_5 = C_2H_2Cl_4 + 2SbCl_3.$$

If the compound of acetylene and antimony pentachloride be heated with an excess of antimony pentachloride, tetrachlorethane alone was obtained.

Sabanejef,[2] eleven years later, repeated this work and obtained very unsatisfactory results. He complained that the absorption took place slowly and

[1] Ann. Chim. Phys. 26, 473, (1872). Carb. D'Hyd. I., 311.
[2] Ann. 216, 261.

with difficulty, that very little heat was evolved, and that explosions often occurred on shaking. He did not succeed in obtaining the crystalline compound mentioned by Berthelot although he had passed the acetylene into the antimony pentachloride for a considerable time.

I have repeated the experiments of Berthelot and Jungfleisch and have come to the same conclusions. Generally, antimony pentachloride absorbed acetylene quite readily, but at times, for some unknown reason, the action at the beginning of the experiment was remarkably slow. I have not found any good cause for the fact. If, however, the contents of the flask be allowed to stand for a day after passing the gas the subsequent action is quite energetic. This fact would seem to show that acetylene is dissolved only in part, that it is not chemically combined, but that combination results on standing for some time. On one occasion acetylene gas was passed for a whole day into the antimony pentachloride with very little result. The next day the gas was again allowed to pass into the compound, and the action was so energetic that it was deemed advisable to cool the flask with water during absorption. This heat was evolved within fifteen minutes from the time that the gas was allowed to enter the apparatus.

The method of Berthelot and Jungfleisch for the preparation of tetrachlorethane, consisted in the distillation of the compound of antimony pentachloride and acetylene, $SbCl_3 \cdot C_2H_2Cl_2$, with an excess of antimony pentachloride. Two molecules of antimony pentachloride gave up four atoms of chlorine with

the formation of tetrachlorethane. This process involved the use of much antimony compound in order to prepare a small quantity of acetylene tetrachloride. If, instead of distilling the compound, $SbCl_3 \cdot C_2H_2Cl_2$, with one molecule of antimony pentachloride, dry chlorine gas was passed into the contents of the flask after previously driving out the gaseous or undissolved acetylene by means of a blast of dry air, the same result could be effected. No explosion took place and the chlorine gas was absorbed with great avidity, and the evolution of so much heat that the flask had to be cooled. The compound, $SbCl_3 \cdot C_2H_2Cl_2$, took up two molecules of chlorine gas, forming tetrachloracetylene and leaving antimony pentachloride according to the reaction:

$$SbCl_3 \cdot C_2H_2Cl_2 + 2Cl_2 = C_2H_2Cl_4 + SbCl_5.$$

Now as antimony pentachloride was again present in the solution, acetylene could be passed into the flask after driving out the excess of uncombined chlorine by means of dry air or some other inert gas. The process of alternately passing the two gases into the compound could be carried on indefinitely. Instead of using the antimony pentachloride as a reagent, it was used rather in the function of "carrier," the same amount of substance being used indefinitely, or even for several separate experiments. It could be obtained unchanged at the end of the operation by distilling off the tetrachlorethane.

The absorption of chlorine was so rapid and perfect, that if the exit-tube be closed, the air was drawn through the safety tube in the chlorine generating

flask, by the diminished pressure due to the rapid absorption of chlorine. Moreover, when the acetylene had been passed alternately several times, its rate of absorption was also improved, and great heat was given off to the reaction. No explosion occurred when the excess of one gas was driven out before passing the other into the apparatus. No more than five minutes was necessary to effect this. When the the absorption of either gas was not allowed to proceed to complete saturation, so that no uncombined gas was present in solution, it was not even necessary to resort to the precaution of using a blast of air to drive out the gas last absorbed. This point of saturation was easily determined by the fact that heat ceased to be evolved when absorption no longer took place.

In one experiment twenty-five grams of antimony pentachloride were treated as above described. A flask with a reflux condenser was used. The latter, however, was not strictly necessary as the products of reaction are not very volatile. A tube bent at right angles was connected with two T-tubes and stop-cocks to admit the gas alternately, likewise one connection with air from blast. The air was dried by passing through a cylinder containing fused calcium chloride. The acetylene was dried by passing through a wash-bottle containing strong sulphuric acid and thence through a drying cylinder containing calcium carbide. The tube bent at right angles through which the gases were introduced into the absorption flask, was drawn out of the liquid before passing each gas, so that in case the previous gas were not perfectly

eliminated by the air-blast, no loss of substance would be sustained by the slight explosion that might occur, forcing the contents back by the concussion. Explosions only occurred when either gas was passed in longer than necessary, that is, after it ceased to be absorbed. Dissolved uncombined gases were with difficulty removed. Chlorine could however, be removed by adding a small quantity of antimony trichloride, and acetylene with antimony pentachloride, if one could not wait until the gases were driven out with the air-blast. Only when changing the gases, and then only when not perfectly eliminated did the introduction of one or the other, cause slight explosion.

In the experiment in question, after passing the acetylene and chlorine alternately several times, the net increase in weight amounted to forty-six grams. The product was distilled, and pure tetrachlorethane obtained. No trace of dichloracetylene, $C_2H_2Cl_2$, was found. No impurities were present after the distillate had been washed with strong hydrochloric acid and water. The product was washed with hydrochloric acid in order to remove a small quantity of antimony pentachloride that came over in the distillation. The oil was dried over fused calcium chloride and possessed the odor of chloroform. It had the correct boiling point of tetrachlorethane.

Another experiment was performed with two hundred grams of antimony pentachloride. The operation was continued until a net increase of 840 grams was obtained from the initial 200 grams of antimony pentachloride. It was not deemed advis-

able to allow the operation to go so far, as it became more difficult to obtain good action when the antimony pentachloride was diluted with four times its weight of tetrachlorethane. It was also more difficult to drive out the acetylene gas which tended to dissolve in great quantity in the tetrachlorethane without entering into chemical combination. The alternating action, however, seemed to go on indefinitely.

According to the method of preparing tetrachlorethane proposed by Berthelot and Jungfleisch, explosions were not altogether eliminated. I have not had explosions except when the gases were changed, and then very rarely. When one gas was carefully drawn out before introducing the other, no explosion ever took place. (The perfect elimination of gas with a blast of air became difficult only when the increase of weight was great, owing to the state of dilution of the antimony pentachloride.) When the product was finally to be distilled, chlorine was passed into the solution for the last time. Explosions were thus avoided which are due to the separation of free acetylene in the presence of free chlorine.

In the distillation some antimony pentachloride passed over with the tetrachlorethane. This was removed with strong hydrochloric acid. Nitric acid did not insure so pure a product. The oil was next washed with water to free it from hydrochloric acid. It was then dried with fused calcium chloride and redistilled. The distillate possessed a constant boiling point to the last few drops within the fraction of a degree and was clear colorless

oil with pure odor. No traces of acid fumes or unpleasant odors were noticed when the products had been sufficiently dried. Acetylene tetrachloride could thus be formed in any desirable quantity. By using larger quantities of antimony pentachloride at the start, even a more perfect action could be obtained, as the heat of the mass-reation greatly promotes absorption. In fact the two gases could be passed simultaneously into a suitable vessel provided they did not come in contact in the gaseous state.

Instead of distilling off the tetrachlorethane, the contents of the flask may be decomposed in water. A white precipitate is thrown down, which is probably a compound of acetylene chloride with antimony chloride or oxychloride, or the crystals of the compound, $SbCl_3 \cdot C_2H_2Cl_2$, insoluble in water. These are treated with strong hydrochloric acid to remove the antimony when the oil reappears. After washing several times with hydrochloric acid, and shaking the oil well in a separating funnel with hydrochloric acid, the tetrachlorethane is washed with water, dried, and distilled.

Berthelot and Jungfleisch seemed to have been of the opinion that the product of the reaction of acetylene upon antimony pentachloride was decomposed by water.[1] The product of the reaction of acetylene upon antimony pentachloride was not destroyed by water. As soon as it was poured into water, a heavy precipitate was thrown down that is not the oxychlo-

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[1] Ann. Chim. Phys. 4, XXVI., (1872).—Carb. D'Hyd. I., 312.

ride of antimony, but a compound of acetylene tetrachloride and antimony chloride, or oxychloride. As I have already stated, tetrachlorethane can be obtained from it by treating it with strong acids. Even when the product obtained by the continued action of chlorine and acetylene upon antimony pentachloride was decomposed, no oil was separated on pouring into water, but a heavy precipitate came out. Whether this be the compound, $SbCl_8 \cdot C_2H_2Cl_2$, referred to by the authors, I have not as yet been able to ascertain with absolute certainty.

The precipitate could be dried in a dessicator, and when subsequently treated with acids gave back the oil. Moreover, the precipitate dissolved in ether, alcohol, or a mixture of ether and alcohol, becoming a clear solution with a gray fluorescence. Antimony oxychloride will not dissolve in these solvents. The ethereal solution of the compound was evaporated to a small volume and crystals reappeared. When chlorine was passed over them, they appeared to absorb it with the evolution of heat, so that the process of chlorination could be continued with the product supposed by Berthelot to be decomposed in water. This fact let to the opinion that the precipitate formed when the product of reaction of acetylene upon antimony pentachloride was poured into water, was not a decomposition product, but a definite compound of acetylene with antimony chloride in an amorphous state. It was the undecomposed product of union between acetylene and antimony pentachloride from which tetrachlorethane was easily recovered with strong acids. In fact

the compound was simply precipitated, not decomposed by water. When attempts were made to dry it for analysis, it continued to give off vapors of tetrachloracetylene and could not be dried to constant weight.

A simple method of preparing any desirable quantity, has been developed in this laboratory. Dry acetylene is passed into antimony pentachloride contained in a flask with a two-holed stopper. The gas is brought into the flask through a tube bent at right angles and dipping below the liquid. The excess of gas escaped by another tube. No reflux condenser is necessary. When the antimony pentachloride is nearly saturated with acetylene, the excess of free gas is either blown out with dry air, or in drrwn through by aspiration. Chlorine is then passed into the flask, until the heat of reaction ceases when acetylene is again introduced after removing any free chloride gas present. This process is continued until the net increase in weight amounts to three times the weight of antimony pentachloride used at the beginning of the experiment. The product is distilled, the distillate washed with strong hydrochloric acid to remove antimony compounds from the oil, then washed with water to remove the acid. It is then dried with fused calcium chloride or sodium sulphate, and redistilled, when pure tetrachlorethane is obtained.

According to the method of preparing tetrachlorethane proposed by Berthelot and Jungfleisch, only eight parts of acetylene can be absorbed by every hundred parts of antimony pentachloride by weight

when the operation must be interrupted. Accordingly in the experiment described, twenty grams of antimony pentachloride would give an increase of only two grams, yielding seven grams of tetrachlorethane. I obtained forty-one grams increase after passing the two gases alternately several times, and over fifty grams of pure tetrachlorethane resulted. Likewise, though according to Berthelot's method, 200 grams of antimony pentachloride should give only 18 grams increase in weight, with the subsequent yield of fifty four grams of tetrachloracetylene, I have obtained a net increase of eight hundred and forty grams which corresponds nearly to a kilogram of tetrachloracetylene, before the operation was discontinued.

REACTION OF ACETYLENE WITH ACIDIFIED MERCURIC FLUORIDE

Acetylene forms two series of compounds with salts of mercury. Carbides are combinations of carbon with a metal, and mercury, like some of the other heavy metals gives a carbide when alkaline solutions of its salts are treated with acetylene. The carbides are generally explosive and on treatment with acids give off acetylene. The other series of acetylene compounds of mercury are not generally explosive, and do not give off acetylene with dilute acids but evolve acetaldehyde when heated in acids. Moreover, whereas the carbides give di-iodacetylene and tetra-iodoethylene when treated with iodine, the non-explosive products obtained from acid or neutral solutions of salts generally appear to yield iodoform. They have been characterized as substituted aldehydes or alcohols, and they contain the metal or an acid-radicle with the metal in the place of one or more of the hydrogen atoms of the organic compound.

The vinyl derivatives of mercury have been extensively studied by Polleck and Thümmel.[1] They gave off acetaldehyde when attempts were made to obtain free vinyl alcohol in a pure state.

In 1866, Berthelot[2] first obtained the carbide of mercury resulting from the action of acetylene on an alkaline solution of a mercury salt. He did not,

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[1] Ber. 22, (1889), 2863.

[2] Ann. Chim. Phys. 4, 9, 386.

however, analyze the product at the time though he noticed its explosive properties. The acetylide was made by passing the acetylene into a solution of mercuric iodide in potassium iodide made alkaline with ammonia.

Basset[1] obtained the same compound from Nessler's solution, but his acetylene appeared to have been impure. He ascribed to it the formula, $C_2H,HgI.,HgO$.

Keiser[2] repeated the experiment of Basset with pure acetylene and his results indicated that the product of the reaction of the gas upon the solution of mercuric iodide and potassium iodide in potassium hydroxide, had the formula, C_2Hg, and is perfectly analogous to the carbides of the other metals, such as silver or copper.

In 1892, Plimpton[3] published a preliminary notice of his work upon this compound, but it was not until 1894 that an extended study of the subject was completed. In 1894, Travers and Plimpton[4] had prepared the explosive carbide of mercury in a number of others ways. In reference to Keiser's work they intimated that they could not obtain the silver compound free from water, and they gave it the formula, $3C_2Hg.H_2O$.

A series of quite different compounds was obtained when acetylene was passed into acid or neutral solution. Kutscherow,[5] in 1883, noticed that allylene

[1] Zeit. f. Chim. (1869), 314, and Chem. News, 19, 28.
[2] Amer. Chem. Jour. 15, 535.
[3] Proc. Roy. Soc. (1894).
[4] Chem. News, 69, 81 and 82, 1 Cent. (1894), 549.
[5] Ber. 17, 13.

and acetylene passed into mercuric chloride gave precipitates. He analyzed the allylene product but does not seem to have made an analysis of the acetylene derivative. Peratoner[1] gave it the formula, $C_2H_2,3HgCl_2,HgO$.

Keiser,[2] however, obtained different results. He found that the compound contained mercurous mercury and that calomel was a product of decomposition on heating. Though not able to separate all the water, he claimed that its composition is represented by the formula, $C_2(HgCl)_2$, or as he also gives it, $C_2(HgCl)_2+\frac{1}{2}H_2O$.

Plimpton[3] had obtained an inexplosive compound by treating mercuric acetate with acetylene. A white precipitate was obtained that turns gray towards the end of the precipitation. The composition of the compound was held to be $3HgO.2C_2H_2$, and the author claimed to be analogous to the allylene compound obtained by Kutscherow $3HgO, 2C_3H_4, 2HgCl_2$. Iodoform was obtained with iodine and aldehyde with dilute acids.

Berge and Reychler[4] had intimated that acetylene was not absorbed by an acid solution of mercuric chloride, and that accordingly this could be used to purify acetylene.

Biginelli[5] proved that acetylene was absorbed by Berge and Reychler's solution with the formation of

[1] Gaz. XXIV., II., (1894), p. 42.

[2] Amer. Chem. Jour. 15, 535.

[3] Proc. Chem. Soc. (1892), 109.

[4] Bull. Soc. Chim. 3, 17, 218.

[5] Ann. di Farm. e Chim. (1898), 16. Cent. (1898), 925.

the definite compound Cl:CH(HgCl), and from this other substances could be obtained by various reactions. It gave aldehyde when heated in dilute acid solution.

Hofman[1] in 1898, obtained from acidified mercuric nitrate, a substance of the composition, $C_2Hg_2NO_4H$. As he obtained the same substance by the action of acetaldehyde on acid mercuric nitrate, he gave the acetylene compound the constitutional formula, $C(Hg)(HgNO_3)CHO$, so that he considered it a substituted aldehyde. He showed that it contained the nitrate group and that it gave aldehyde with dilute acids.

Erdman and Köthner[2] tried the action of acetylene on mercurous nitrate, and obtained a compound of the formula, $C_2(Hg_3NO_3)+H_2O$. They also succeeded in obtaining a method for the continuous preparation of aldehyde from acetylene by passing the gas into a boiling solution of sulphuric acid to which mercuric oxide or a mercury salt has been added. Köthner[3] referred to the fact that he had obtained a compound of acetylene with mercuric nitrate, and had given it the formula, $C_2Hg_3NO_4H_2$, or as it was afterwards shown to be, HgC:CHg+$HgNO_3+H_2O$. He claimed, moreover, to have shown its relation to acetaldehyde and vinyl alcohol, before the article of Hofman had appeared.

Hofman[4] criticised Erdman and Köthner's work on

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[1] Ber. 31, 2475.
[2] Zeit. An. Chem. 18, 48.
[3] Ber. 31, 2475.
[4] Ber. 31, 2783.

the ground that, if they had known the relation of the mercury compound to acetaldehyde, they would not have given it an acetylide formula. Hofman claimed that the product of acetylene with acidified mercuric nitrate was neither an acetylide nor a mercurous compound, but a substituted aldehyde. He repeated some of his previous experiments with the same results that he had obtained before, and he gave the compound the aldehyde formula:

$$\begin{matrix} NO_3Hg \\ OHg_2 \end{matrix} > C < \begin{matrix} H \\ O. \end{matrix}$$

I have attempted to prepare, among others, the fluoride of acetylene and mercury by passing the gas into an acidified solution of mercuric fluoride. Freshly precipitated mercuric oxide was dissolved in cold concentrated hydrofluoric acid. The oxide dissolves readily with the evolution of heat when the vessel is shaken so that it is necessary to cool the beaker. All the glass apparatus used was well coated with paraffine to prevent corrosion, and also in order to prevent the subsequent introduction of silica as an impurity in the precipitated mercury fluoride of acetylene. When no more mercuric oxide dissolved in the acid, a stream of acetylene was passed into the clear filtered solution. A white flaky precipitate was immediately formed. At a certain stage of the reaction the precipitate began suddenly and quickly to turn grayish or bluish white. In order to obtain the white compound free from the gray precipitate the mixture was filtered every few minutes until the product began to change. The stream of gas was

then continued until the precipitation ceased. Both compounds were separately washed with strong hydrofluoric acid. They were then washed with alcohol to remove water and finally with ether to take out any alcohol remaining. The compounds were then dried over sulphuric acid in a dessicator for several weeks to a constant weight. The white compound is somewhat soluble in strong hydrofluoric acid, insoluble in water, alcohol, or ether. It is a light white powder resembling the product of the action of acetylene on neutral mercuric chloride, $C_2(HgCl)_2$, examined by Keiser.

ANALYSIS OF THE WHITE PRECIPITATE.

.4834 grams of substance gave .4739 grams of Mercuric Sulphide.

.6435 grams of substance gave .6298 grams of Mercuric Sulphide.

PERCENTAGE OF MERCURY.

Calculated for	$C_2(HgCl)_2$,	Found
Hg.	82.2	I.—82.7
		II.—82.4

The gray compound resulted from the continued action of acetylene on acidified mercuric fluoride. It resembled in nearly every respect the white compound. Towards the end of the reaction free acetaldehyde was present.

ANALYSIS OF THE GRAY PRECIPITATE.

.4834 grams of the compound gave .4041 grams of Mercuric Sulphide.

.6435 grams of the compound gave .6298 grams of Mercuric Sulphide.

Calculated for	$C_2(HgF)_2+H_2O$ or $CH(HgF){:}C(HgF){\cdot}OH$	Found
Hg.	83 3	I.—83.6
		II.—84.3

These compounds are insoluble in dilute acids, and soluble in warm concentrated nitric acids with the formation of mercurous nitrate. Caustic potash precipitates from the diluted nitric acid solution mercurous oxide. When hydrogen sulphide is passed into the compounds suspended in water, they turn black and acetaldehyde and thioaldehyde are formed. Acetaldehyde and thioaldehyde are also formed when the substances are treated with ammonium sulphide, and then neutralized with hydrochloric acid. With concentrated hydrochloric acid a strong reaction takes place with the evolution of hydrofluoric acid, and the formation of the compound, $C_2(HgCl)_2$, analyzed by Keiser.

$$C_2(HgF)_2+2HCl=C_2(HgCl)_2+2HF.$$

Dry bromine reacts so energetically with the substance that the latter is carbonized on contact. Bromine water gives rise to traces of an oil that is probably bromoform, or bromacetylene. Dry chlorine also decomposes the mercury acetylene fluoride with the evolution of much heat, and the formation

of a small amount of oil. The products resulting from the action of bromine and chlorine have not been carefully studied. A solution of iodine and potassium iodide gives rise to iodoform. A better yield of iodoform is obtained by boiling the compound with iodine and sodium carbonate. The iodoform was very pure and after its first crystalization from alcohol melted exactly at 119°C.

The acetylene compound of mercuric fluoride dissolves in chloric acid, or potassium chlorate and hydrochloric acid, and mercuric chloride is obtained. The fact that the mercury in the compound is in the mercurous condition, and that the substance readily unites with water in the presence of dilute acids giving rise to acetaldehyde, seems to point to the fact that it may be a substituted aldehyde of the formula, $CH(HgF)_2CHO$. It may also be a substituted vinyl alcohol which also would give rise to acetaldehyde when decomposed. The production of iodoform also indicates this. The mode of formation of the compound may be represented as follows:

$$C_2H_2+2HgF_2=C_2(HgF)_2+2HF, \text{ or,}$$

$$C_2(HgF)_2+HOH=CH(HgF){:}C(HgF)OH \text{ or,}$$

$$CH(HgF)_2CHO.$$

The formation of acetaldehyde from the compound is represented thus.

$$CH(HgF){:}C(HgF)OH+2HF=(CH_2{:}CHOH)+$$

$$2HgF_2,$$

$$(CH_2{:}CHOH)=CH_3CHO.$$

There is more evidence in favor of the vinyl alcohol formula for the compound. If the mercury derivative had an aldehyde formula it would probably be likely that it could be formed from acetaldehyde and mercuric fluoride solution. Acetaldehyde does not react with mercuric fluoride with the formation of a precipitate.

It is most likely then a vinyl derivative that gives off acetaldehyde when decomposed. It is analogous to the vinyl mercury derivatives prepared by Polleck and Thümmel.

Keiser's compound, $C_2(HgCl)_2+H_2O$ is none other than the product, $CH(HgCl):C(HgCl)OH$ prepared by Polleck and Thümmel from ether derivatives.

In conclusion I wish to thank Mr. W. Waggaman for his kind assistance in supplying me with the electrodes of calcium carbide used in the electrolytical experiments. I thank him also for assisting me to set up the apparatus, etc.

Notre Dame, Indiana,
October, 1904.

BIOGRAPHICAL.

Julius A. Nieuwland was born near Ghent, Belgium, February 14, 1878. In 1880, his parents came to the United States, and settled in South Bend, Ind. His first instruction was received in St. Mary's parochial school in that place. In September, 1892, he entered the preparatory courses at Notre Dame University, and was graduated with the degree of Bachelor of Arts in 1899. After a novitiate in the Congregation of Holy Cross, at Notre Dame, Ind., he entered Holy Cross College, Washington, D. C., where he pursued his theological studies. He was ordained to the priesthood December 19, 1903. Having entered the Catholic University of America in 1900 as a graduate student in the Faculty of Philosophy he followed the course of chemistry as a major subject, and botany, experimental psychology and biology as subordinate studies.

INDEX.

PART I.

PART II.

1ST DIVISION.

APPENDIX.

ERRATA.

On page 17, line 19, read "water" for "the anhydride."
On page 67, line 16, put "(C)" for "(G)."
On page 67, line 27, for "tighty" read "tightly."
On page 83, line 1, for "derivities" read "derivatives."
On page 95, line 3, in title, put "reaction" for "reation."
On page 100, line 15, read "retarded ' for "retarted."
On page 113, line 1, insert "to" after "due," to read "This was probably due to," etc.
On page 121, line 9, read "ordinary" for "oridinary."


Chem 479.04.3
Some reactions of acetylene ...
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